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(54) Title: SULFUR TRAP IN NO<sub>x</sub> ADSORBER SYSTEMS FOR ENHANCED SULFUR RESISTANCE

(57) Abstract: An exhaust gas catalyst system, comprises: a sulfur trap warm-up catalyst, housed within the exhaust stream and comprising: a sulfur scavenger component; and a NO<sub>x</sub> adsorber catalyst, housed within the exhaust stream downstream from said sulfur trap in an underfloor position. The method of reducing sulfur poisoning of a nitrogen oxide adsorber, housed within an exhaust gas catalyst system, comprises: placing a sulfur trap within the exhaust stream upstream from a NO<sub>x</sub> adsorber, wherein said sulfur trap comprises: a sulfur scavenger component.

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## SULFUR TRAP IN NO<sub>x</sub> ADSORBER SYSTEMS FOR ENHANCED SULFUR RESISTANCE

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims the benefit of the Provisional Application Serial Number 60/178,927 filed February 1, 2000, which is hereby incorporated by reference.

### TECHNICAL FIELD

The present disclosure relates to nitrogen oxide adsorption materials used in exhaust systems of internal combustion engines.

### BACKGROUND

It is well known in the art to use catalyst compositions, including those commonly referred to as three-way conversion catalysts ("TWC catalysts") to treat the exhaust gases of internal combustion engines. Such catalysts, containing precious metals like platinum, palladium, and rhodium, have been found both to successfully promote the oxidation of unburned hydrocarbons (HC) and carbon monoxide (CO) and to promote the reduction of nitrogen oxides (NO<sub>x</sub>) in exhaust gas, provided that the engine is operated around stoichiometry balanced for combustion ("combustion stoichiometry"; i.e., an air to fuel (A/F or  $\lambda$ ) ratio of about 14.7 and 14.4, in the case of a gasoline engine).

Fuel economy and global carbon dioxide (CO<sub>2</sub>) emissions have made it desirable to operate the engine under lean-burn conditions, where the A/F ratio is somewhat greater than combustion stoichiometry (i.e., greater than 14.7 and generally between 19 and 35), to realize a benefit in fuel economy. When lean-burn conditions are employed, three way catalysts are efficient in oxidizing the unburned hydrocarbons and carbon monoxides, but are inefficient in the reduction of nitrogen oxides.

One approach for treating nitrogen oxides in exhaust gases of engines operating under lean-burn conditions has been to incorporate NO<sub>x</sub> adsorbers in exhaust lines along with three-way catalysts. Conventional exhaust systems contemplate any number of configurations, including for example, use of NO<sub>x</sub> adsorbers in the same canister along with three-way catalysts or use of a NO<sub>x</sub> adsorber in a separate can upstream of the three-way catalyst, among others.

These adsorbers generally comprise a catalytic metal, such as platinum, palladium and/or rhodium, in combination with an alkali and/or alkaline earth element (hereinafter the "alkali material"), loaded on a porous support such as alumina, gamma-alumina, zirconia, alpha-alumina, cerium oxide (ceria), or magnesium oxide. The catalytic material in the adsorber acts first to oxidize NO to NO<sub>2</sub>. NO<sub>2</sub> then reacts with the alkali and alkaline earth materials to form stable nitrate salts. In a stoichiometric or rich environment, the nitrate is thermodynamically unstable, and the stored NO<sub>x</sub> is released for catalysis, whereupon NO<sub>x</sub> is reduced to N<sub>2</sub> gas.

For practical incorporation of the supported catalytic materials into internal combustion engine exhaust systems, the support will, itself, be deposited on a chemically stable and thermally insulating substrate, or metallic substrate. Particularly useful substrates include cordierite and mullite, among others. The substrate may be of any size or shape, such as is required by the physical dimensions of the designed exhaust system. Similarly, the internal configuration of the substrate may be any known or commonly employed configuration. Substrates are typically formed as monolithic honeycomb structures, layered materials, or spun fibers, among other configurations.

U.S. Patent No. 5,727,385 to Hepburn, which is herein incorporated by reference, discloses a NO<sub>x</sub> trap, comprising (i) at least one precious metal selected from platinum and palladium loaded on a porous support; and (ii) at least one alkali or alkaline earth metal (a) loaded on a porous support or (b) present as an oxide thereof. Hepburn optionally includes a three-way catalyst located either between the two components or after the NO<sub>x</sub> trap.

Although the NO<sub>x</sub> adsorbers remove the NO<sub>x</sub> from the exhaust stream during lean burn conditions and/or low temperatures, they are plagued with the problem of sulfur poisoning under such conditions. Sulfur, a contaminant present in fuel, adsorbs onto the NO<sub>x</sub> adsorber, reducing the sites available for trapping NO<sub>x</sub>.

What is needed in the art is an exhaust gas catalyst system having improved durability, as well as NO<sub>x</sub> and sulfur management, over extended operating time.

## SUMMARY

The above-described and other disadvantages of the prior art are overcome by an exhaust gas catalyst system. The exhaust gas catalyst system comprises: a sulfur trap disposed within an exhaust stream, said sulfur trap comprising a sulfur scavenger component; and a NO<sub>x</sub> adsorber catalyst disposed within the exhaust stream, downstream from said sulfur trap.

The above-described and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description, drawings, and appended claims.

## BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the accompanying drawings, which are meant to be exemplary, not limiting, and wherein like elements are numbered alike in the several Figures, in which:

Figure 1 is a graphic representation of sulfur concentration vs. adsorption time, showing fresh sulfur adsorption of a sulfur trap at 400°C and an A/F ratio of 20, with 100ppm (parts per million) sulfur dioxide (SO<sub>2</sub>). High sulfur adsorption efficiency for the sulfur trap is established.

Figure 2 is a graphic representation of sulfur concentration vs. release time, showing fresh sulfur release from a sulfur trap at 700°C and an A/F ratio of 13, following exposure to sulfur as depicted in figure 1. High sulfur regenerability for the sulfur trap is established.

Figure 3 is a graphic representation of sulfur concentration vs. adsorption time, showing sulfur adsorption of a fresh sulfur trap as a function of temperature (200-700°C lines) at high space velocity. High sulfur adsorption efficiency across a wide temperature window for the sulfur trap is established.

5                Figures 4 and 5 shows graphic representations of sulfur concentration vs. release time, showing sulfur release from a fresh sulfur trap at 600°C (Figure 4) and at 700°C (Figure 5) with an A/F ratio of 13, 13.6 and 14 after adsorption with 100 ppm SO<sub>2</sub> at 400°C for 40 minutes. Regenerability of the sulfur trap is established.

10              Figures 6 and 7 shows graphic representations of sulfur concentration vs. adsorption time at 400°C for 40 minutes at an A/F ratio of 20 (Figure 6) and sulfur concentration vs. release time at 700°C for 10 minutes with an A/F ratio of 13, (Figure 7). Establishes good sulfur storage and good sulfur release after repeated sulfur poisoning and regeneration.

15              Figure 8 is a graphic representation of sulfur concentration vs. adsorption time at 400°C for 40 minutes at an A/F ratio of 20 (with 100 ppm SO<sub>2</sub> in feed gas) of a fresh and two aged warm-up catalysts, aged at 900°C and 950°C for 16 hours in air and water.

20              Figure 9 is a graphic representation of sulfur concentration vs. adsorption time for fresh and aged sulfur trap warm-up catalysts at different flow rates (SV = 45,000 to 90,000 per hour). High sulfur trap efficiency at modest flow rate for the fresh and aged warm-up catalysts is established.

25              Figure 10 is a graphic representation of sulfur concentration vs. release time, showing sulfur release at 700°C and  $\lambda$  of 13 from a fresh and two thermally aged sulfur traps after sulfur adsorption at 400°C for 40 minutes and an A/F ratio of 20 with 100 ppm SO<sub>2</sub>.

30              Figure 11 is a graphic representation of NO<sub>x</sub> adsorption performance of the sulfur trap at 300°C vs. adsorption time, showing NO<sub>x</sub> adsorption of fresh and aged (at 900°C or 950°C) sulfur trap warm up catalyst. Establishes that the sulfur trap provides a modest NO<sub>x</sub> trapping function.

Figure 12 is a graphic representation of NO<sub>x</sub> conversion percentage vs. evaluation temperatures, showing NO<sub>x</sub> conversions of fresh and aged (at 900°C or 950°C) sulfur trap at high SV. Establishes that the sulfur trap provides a modest NO<sub>x</sub> conversion function.

5                    Figure 13 is a graphic representation of sulfur concentration vs. release time at 700°C, and at an A/F ratio 13, of an aged (900°C in air) sulfur trap for palladium, palladium/platinum, and palladium/ platinum/rhodium precious group metal loadings.

10                    Figure 14 is a graphic representation of NO<sub>x</sub> adsorption percentage at 300°C of NO<sub>x</sub> adsorbers with and without sulfur trap protection.

Figure 15 is a graphic representation of NO<sub>x</sub> conversion percentage at (30 seconds lean/2 seconds rich) of NO<sub>x</sub> adsorbers with and without sulfur trap protection.

15                    Figure 16 shows a simple scheme for an exhaust gas catalyst system, comprising a sulfur trap, located in close coupled position with an internal combustion engine, and a NO<sub>x</sub> adsorber, placed in underfloor position.

Figure 17 shows a more complex scheme for an exhaust gas catalyst system in a diesel engine, further comprising a particulate trap.

20                    Figure 18 is a graphical illustration of transmittance of sulfur through a NO<sub>x</sub> adsorber during continuous regeneration.

Figure 19 is a bar graph illustrating that after severe aging at 995°C maximum bed temperature for 100 hours, start up catalysts with (lines 16,18,20) and without (lines 15,17,19) sulfur scavengers have substantially equivalent light off performance.

25                    Figures 20 and 21 are graphical illustrations showing lean adsorption and rich release of sulfur from two platinum based sulfur traps, wherein lines 21 and 30 represent temperature, while lines 22 and 31 represent sulfur concentration. Clearly the second formulation (figure 21) releases sulfur at 300°C, and is therefore suitable for a continuous regeneration strategy, while  
30                    the first formulation (figure 20) releases no sulfur at 300°C, and is thus suitable for a periodic regeneration strategy.

Figure 22 is a graphical illustration of the rich and lean adsorption of different sulfur species by a NO<sub>x</sub> adsorber; line 221 represents H<sub>2</sub>S at an A/F of 13, line 222 represents SO<sub>2</sub> at an A/F of 13, and line 223 represents SO<sub>2</sub> at an A/F of 20.

5                    Figure 23 is a graphical illustration of NO<sub>x</sub> adsorber conversion efficiency after aging for 20 hours with no sulfur (line 232) or in the presence of H<sub>2</sub>S (line 233) or SO<sub>2</sub> (line 231) in a rich environment (A/F is 13.2).

                    Figure 24 is a graphical representation of the projection of frequency of sulfur trap regeneration (periodic regeneration strategy) as a  
10                   function of ppm sulfur content in the fuel for two different sulfur trap formulations, both platinum based.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

                    The exhaust gas catalyst system provides improved management of NO<sub>x</sub> and sulfur components through incorporation of a sulfur trap upstream from a NO<sub>x</sub> adsorber, the sulfur trap comprises a sulfur scavenging component  
15                   and optionally an oxidation catalyst and/or a lean NO<sub>x</sub> catalyst.

                    Additionally, the nature of sulfur species released during periodic regeneration, including hydrogen sulfide (H<sub>2</sub>S) or sulfur dioxide (SO<sub>2</sub>), can be tuned depending on the materials utilized to build the sulfur scavenging sulfur trap. The sulfur trap comprises a sulfur scavenging component and optionally a  
20                   catalytic component (NO<sub>x</sub> and/or oxidation catalyst) comprising one or more precious metals, e.g., an oxidation catalyst and/or a NO<sub>x</sub> catalyst, disposed on a substrate. Parameters in selecting sulfur scavenging components for the sulfur trap include the temperatures at which these components release sulfur species and the level of exhaust richness required to trigger such release. These  
25                   parameters may be adjusted to the particular exhaust design, and materials selected, accordingly. The sulfur scavenging component comprises trapping element(s) having a sufficient affinity for sulfur to enable adsorption in a lean exhaust environment (e.g., at an A/F ratio of about 17 and above) and optionally, a support. Materials are also preferably selected on their ability to  
30                   release sulfur at relatively low temperatures under rich exhaust conditions.

Trapping elements including silver (Ag), aluminum (Al), barium (Ba), cerium (Ce), cobalt (Co), copper (Cu), lanthanum (La), lithium (Li), magnesium (Mg), sodium (Na), neodymium (Nd), rubidium (Rb), tin (Sn), strontium (Sr), and zinc (Zn), among others, as well as combinations and alloys comprising at least one of the foregoing elements, have been found to be optimally effective and are accordingly preferred. Combinations of two or more elements are particularly preferred since such combination provides a more balanced adsorption performance over wider A/F ratio and temperature ranges.

The trapping element(s) may be applied to supporting materials as is known in the art. Suitable support materials include high surface area materials (e.g., a surface area of about 50 m<sup>2</sup>/g or greater), such as alumina (gamma-alumina, alpha alumina, theta alumina, and the like), zeolite, zirconia, magnesium oxide, titania, silica, and combinations comprising at least one of the foregoing support materials, among others. Since ceria stores oxygen in lean phases which translates to a fuel economy penalty during lean to rich modulations where storage of O<sub>2</sub> in lean phase consumes additional reductants, ceria within the sulfur trap catalyst should be minimized or eliminated. Desirably, the support material has a surface area above about 300 square meters per gram (m<sup>2</sup>/g).

There are no real upper limits for the amount of sulfur scavenging and/or catalytic components that can or should be loaded onto the support, except in as much as overloading of the support material can cause undesirable backpressures and pressure drops within the exhaust system. Similarly, there are no real lower limits for the amount of sulfur scavenging and/or catalytic components that can be loaded onto the support, it being recognized that the effectiveness of the trapping elements increase as the amount of the trapping elements loaded onto the support increases. Exemplary sulfur scavenging components comprise barium in an amount of up to about 1,480 grams per cubic foot (g/ft<sup>3</sup>); strontium in an amount of up to about 940 g/ft<sup>3</sup>; and magnesium in an amount of up to about 500 g/ft<sup>3</sup>. A particularly preferred sulfur scavenging component designed to provide optimal amounts of



trapping elements while reducing backpressure, comprises a combination of about 370 to about 740 g/ft<sup>3</sup> barium, about 235 to about 375 g/ft<sup>3</sup> strontium, and about 125 to about 250 g/ft<sup>3</sup> magnesium.

For example, a sulfur trap composition could have a catalytic component comprising up to about 95 wt% sulfur scavenging component, up to about 25 wt% catalyst (NO<sub>x</sub> and/or oxidation), and optionally up to about 40 wt% stabilizers, disposed on a substrate; with about 40 wt% to about 90 wt% sulfur scavenging component, about 2 wt% to about 20 wt% catalyst, and about 2 wt% to about 40 wt% stabilizers preferred; and about 60 wt% to about 85 wt% sulfur scavenging component, about 3 wt% to about 10 wt% catalyst, and about 5 wt% to about 30 wt% stabilizers especially preferred; based upon the total weight of the catalytic component. For example the catalytic component of the sulfur trap could comprise about 40 wt% Ba, about 25 wt% Sr, about 6 wt% Ce, about 6 wt% precious metals, and about 23 wt% stabilizers. Alternatively, the catalytic component of the sulfur trap could comprise about 50 wt% Ba, about 32 wt% Sr, about 7 wt% precious metals, and about 11 wt% stabilizers.

To provide structural integrity to the sulfur trap the support is, itself, carried on a high temperature, insulating substrate. Particularly useful substrates, which are stable in high temperatures (e.g., temperatures up to about 1,200°C), include cordierite, mullite, and metal substrates, among others. This substrate, which may be in any known or commonly employed configuration, is typically formed as a monolithic honeycomb structure, layered materials, or spun fibers, among other configurations.

As mentioned above, the sulfur scavenging component obtained may be utilized alone, or combined with precious metals, including palladium, platinum, gold, rhodium, osmium, iridium, and ruthenium, as well as combinations and alloys comprising at least one of the foregoing metals. A preferred sulfur trap catalyst precious metal (PM) loading comprises: up to about 60 g/ft<sup>3</sup> platinum, up to about 250 g/ft<sup>3</sup> palladium, and up to about 30 g/ft<sup>3</sup> rhodium. A particularly preferred sulfur trap catalyst has a PM loading, designed for optimal performance, comprising: about 10 to about 40 g/ft<sup>3</sup>

platinum, about 40 to about 100 g/ft<sup>3</sup> palladium, and about 3 to about 10 g/ft<sup>3</sup> rhodium.

Not to be bound by theory, platinum generally enhances palladium-based light off functions by facilitating nitrogen oxide (NO) to  
5 nitrogen dioxide (NO<sub>2</sub>) and sulfur dioxide (SO<sub>2</sub>) to sulfite (SO<sub>3</sub>) oxidation, thereby improving both NO<sub>x</sub> and sulfur oxides (SO<sub>x</sub>) trapping efficiencies. Rhodium, located on the sulfur trap surface, enhances NO<sub>x</sub> reduction, both at stoichiometry and during lean to rich modulations and also promotes high steady state hydrocarbon conversions. Accordingly, a tri-metallic formulation is  
10 preferred to provide effective storing of NO<sub>x</sub> (to the extent that it occurs in the sulfur trap) and SO<sub>x</sub> and for converting stored NO<sub>x</sub> during lean to rich modulations.

Rhodium addition to platinum and palladium improves sulfur release under rich conditions. Not to be limited by theory, this is believed to be  
15 attributable to enhanced rates of steam reforming, which results in the production of hydrogen (H<sub>2</sub>) gas; a very effective constituent for NO<sub>x</sub> and sulfate reduction. Consistent with this, the tri-metallic formulation is also found to be more effective for the release of sulfur during high temperature rich desulfation than palladium only and platinum/palladium formulations of the  
20 same support architecture. Figure 13 shows that after high temperature aging (900°C in air), the platinum-palladium-rhodium catalyst (line 121) has better sulfur release at 700°C and A/F ratio 13, than the platinum-palladium (line 122) and palladium (line 123) catalysts.

The sulfur trap catalyst itself may be made out of the sole sulfur  
25 scavenger component, or it may be made as a mixture (or juxtaposition) of the sulfur scavenger component and either of an oxidation catalyst or a lean NO<sub>x</sub> catalyst. Where either of the oxidation catalyst or lean NO<sub>x</sub> catalyst accompanies the sulfur scavenging component, the sulfur trap catalyst may be formed by any conventional technique.

30 The one of three main production techniques are preferred. First, all components can be mixed in the same washcoat and applied to the substrate.

Alternately, the sulfur scavenging component and either of the oxidation catalyst or lean NO<sub>x</sub> catalyst can be applied as separate layers (in any order) on the same catalyst brick (monolith). As a third alternative, the components can be banded onto a dual brick system, where the sulfur scavenging component and either of the oxidation catalyst or lean NO<sub>x</sub> catalyst can be applied to separate bricks or separate areas of one brick.

These sulfur traps can be employed in various manners: (a) sulfur trap close-coupled brick and NO<sub>x</sub> adsorber underfloor brick; (b) sulfur trap close-coupled brick and a dual brick underfloor arrangement with the first portion being a sulfur trap and the second portion being a NO<sub>x</sub> adsorber; and (c) sulfur trap close-coupled brick with a NO<sub>x</sub> adsorber underfloor brick with a sulfur trapping function incorporated via the use of the sulfur scavenging components.

Experimentally, the startup catalyst adsorbs sulfur with nearly 100% efficiency at temperatures of about 200°C to about 700°C, whether fresh or after severe thermal aging at about 700°C to about 950°C for 16 hours. The following Figures detail experimental performance characteristics for a sulfur trap catalyst, comprising approximately: 40 g/ft<sup>3</sup> platinum, 80 g/ft<sup>3</sup> palladium, 11 g/ft<sup>3</sup> rhodium, 740 g/ft<sup>3</sup> barium, and 472 g/ft<sup>3</sup> strontium.

Figure 1 shows fresh sulfur adsorption for a sulfur scavenging component at 400°C and an A/F ratio of 20, with 100 ppm (parts per million) SO with sulfur breakthrough, or unadsorbed sulfur, measured in total sulfur mode, in which all species of sulfur are analyzed. In contrast, Figure 2 shows fresh sulfur release for a sulfur scavenging component at 700°C and an A/F ratio of 13. These Figures indicate a high sulfur adsorption and release efficiency for the sulfur scavenging component.

Figure 3 shows sulfur adsorption of a fresh sulfur scavenging component at high space velocity as a function of temperature (200-700°C (the line numbers correlate with the temperatures in °C)). Sulfur breakthrough was measured in total sulfur mode. A new sample was used in each adsorption test. As can be seen in Figure 3, the fresh sulfur scavenging component shows high

sulfur adsorption efficiency across a wide temperature window for the sulfur scavenging component.

Figures 4 and 5 show sulfur release from a fresh sulfur scavenging component at 600°C and at 700°C, respectively, over three A/F ratios, 13 (lines 41, 51), 13.6 (lines 42, 52), and 14 (lines 43, 53), after adsorption with 100 ppm SO<sub>2</sub> at 400°C for 40 minutes. Temperature was ramped up to 600°C or 700°C in nitrogen gas, whereupon synthetic gas simulating exhaust, at the particular A/F ratio, was switched online for 10 minutes. Sulfur emission was measured in total sulfur mode. Figures 4 and 5 show that the sulfur scavenging component is regenerable.

Figures 6 and 7 show sulfur adsorption of a fresh sulfur scavenging component at 400°C at an A/F ratio of 20 and 100ppm SO<sub>2</sub> for 40 minutes (Figure 6) and sulfur release of a fresh sulfur scavenging component at 700°C at an A/F ratio of 13 and 100ppm SO<sub>2</sub> for 10 minutes (Figure 7). Sulfur breakthrough was measured in total sulfur mode. Figures 6 and 7 show good sulfur storage and release performance after repeated sulfur poisoning and regeneration.

Figure 8 shows sulfur adsorption at 400°C of a fresh (line 73) and of two aged (900°C (line 72) and 950°C (line 71) for 16 hours in air and water) sulfur trap catalysts at an A/F ratio of 20 for 40 minutes (100 ppm SO<sub>2</sub> in feed gas). Good adsorption performance of fresh and aged sulfur scavenging components is established.

Figure 9 shows sulfur adsorption at 400°C, A/F ratio of 20 and 10ppm SO<sub>2</sub> for fresh (line 82) and 900°C aged (lines 81 and 83) sulfur trap catalysts at different flow rates, 45,000 (line 83 (1 inch (") by 1")) and 90,000 per hour (line 81 (1" by 0.5"); line 82 (1" x 0.5")). This figure indicating a high sulfur trap efficiency at modest flow rate for both the fresh and aged catalysts.

Figure 10 shows sulfur release at 700°C and an A/F ratio of 13 from a fresh (line 93) and two thermally aged (900°C, line 92 and 950°C, line 91) sulfur scavenging components after sulfur adsorption at 400°C at an A/F ratio of 20, for 40 minutes with 100 ppm SO<sub>2</sub>. Temperature was ramped up to

700°C under nitrogen gas, whereupon rich gas was switched online for 10 minutes. Sulfur emission was measured in total sulfur mode. Figure 10 further establishes that the thermally aged sulfur scavenging component is regenerable.

As mentioned above, the sulfur scavenging component may additionally possess some NO<sub>x</sub> adsorption and conversion properties. Figure 11 shows NO<sub>x</sub> adsorption of fresh (line 101) and aged sulfur scavenging components (line 102 aged at 900°C in air/H<sub>2</sub>O; line 103 aged at 950°C in air/H<sub>2</sub>O) at high space velocity ("SV", which is the flow of exhaust gas over the catalyst in one hour divided by the catalyst volume) of 61,000 hr<sup>-1</sup>, showing that the sulfur scavenging components provide a modest NO<sub>x</sub> trapping function. For the sulfur scavenging component in Figure 11, the component was aged at 900°C (line 102) or 950°C (line 103) in air and water for 16 hours.

Figure 12 shows NO<sub>x</sub> conversions of fresh (line 111) and aged sulfur scavenging components (line 112 aged at 900°C C in air/H<sub>2</sub>O; line 113 aged at 950°C C in air/H<sub>2</sub>O; both for 16 hours) at high SV, showing that the sulfur scavenging components provide a modest NO<sub>x</sub> conversion function. For Figure 12, NO<sub>x</sub> conversions were plotted at different temperatures for fresh and aged sulfur scavenging component at a SV of 61,000 per hour, with 500 ppm of NO<sub>x</sub> and with 30 second to 2 second lean to rich modulations.

Experimentally, the sulfur trap exhibits light-off performance equivalent to that of standard three-way catalysts of comparable precious metal (PM) loading. The sulfur trap also provides reasonable levels of NO<sub>x</sub> conversion and acceptable NO to NO<sub>2</sub> oxidation efficiencies even at high space velocities (e.g., SV of up to about 60,000 hr<sup>-1</sup>), such performance being dependent on PM loadings, aging conditions, catalyst volumes, among other parameters. Experimental values showed 8% NO to NO<sub>2</sub> oxidation for fresh sulfur scavenging component and 1% NO to NO<sub>2</sub> oxidation for sulfur scavenging component aged at 900°C in air and water.

Because the sulfur trap is proximal to the engine, NO<sub>x</sub> conversion over the sulfur trap catalyst occurs before the temperature at the underfloor location is sufficient to fully adsorb NO<sub>x</sub> species. As a result,

overall system performance is enhanced. Further, NO to NO<sub>2</sub> oxidation over the sulfur trap also improves NO<sub>x</sub> trapping efficiency on the downstream NO<sub>x</sub> adsorber. The desulfation of this sulfur trap catalyst is also facilitated when it is closely proximal to the engine manifold, where it is exposed to higher average exhaust temperatures, allowing at least partial sulfur regeneration under modest driving conditions.

The NO<sub>x</sub> adsorber used in conjunction with the sulfur trap may be any NO<sub>x</sub> adsorber as can be found in the prior art. The NO<sub>x</sub> adsorber should comprise a catalyst capable of catalyzing NO<sub>x</sub> under rich conditions and a material capable of adsorbing NO<sub>x</sub> under lean conditions. Typically, the NO<sub>x</sub> adsorber comprises catalyst, such as a precious metal, metal oxide, alkali and/or alkaline earth metal, disposed on a support such as alumina, titania, zirconia, ceria, lanthanum oxide, zeolite, silica, magnesia or a combination comprising at least one of the foregoing. An exemplary NO<sub>x</sub> adsorber is described in U.S. Patent No. 5,727,385 to Hepburn, which discloses a NO<sub>x</sub> adsorber, comprising: (i) at least one precious metal selected from platinum and palladium loaded on a porous support; and (ii) at least one alkali or alkaline earth metal (a) loaded on a porous support or (b) present as an oxide thereof.

In one embodiment, the sulfur trap is employed upstream of a NO<sub>x</sub> adsorber located in an underfloor position in any type of exhaust system, including diesel. Consequently, the NO<sub>x</sub> adsorber is protected from sulfur poisoning in the first instance, and purged of sulfur buildup when required.

The sulfur trap and NO<sub>x</sub> adsorber may simultaneously adsorb, during lean phases, and release, during rich pulses, sulfur species and NO<sub>x</sub> species, in which case the sulfur maintenance strategy is referred to as continuous regeneration mode. Figure 21 shows a sulfur trap component consistent with continuous regeneration, i.e. capable of releasing sulfur at low temperature (300°C).

However, a system whereby the sulfur scavenging component would adsorb sulfur species for an extended period of time, regardless of the A/F ratio, at low temperature (between about 200°C to about 500°C), and then

release sulfur during events specifically aimed towards sulfur trap regeneration (for example, longer rich periods at temperatures of about 500°C to about 700°C or more), is preferred as is supported by Figures 20, 22 and 23. Figure 22, as well as Figure 23, show that in the rich mode, much less sulfur is adsorbed on a NO<sub>x</sub> adsorber than in the lean mode. Essentially, if sulfur is trapped upstream from a NO<sub>x</sub> adsorber in the lean mode, and then released from the sulfur trap in the rich mode; since the NO<sub>x</sub> adsorber has much less capacity for sulfur in the rich mode, poisoning of the NO<sub>x</sub> adsorber will be less severe. In fact, as is illustrated by the dashed lines in Figures 16 and 17, if the NO<sub>x</sub> adsorber is bypassed during the rich releases of sulfur, poisoning would be completely eliminated. The periodic strategy is preferred to the continuous strategy because less sulfur releases mean less opportunities for the sulfur to readsorb on the downstream NO<sub>x</sub> adsorber and thus slower poisoning of the NO<sub>x</sub> adsorber.

With reference to Figure 16, for example, the exhaust gas system comprises a sulfur trap (3), located within the exhaust stream and a NO<sub>x</sub> adsorber (4) downstream of the sulfur trap (3), in an underfloor position. As discussed above, depending on the application, the sulfur trap (3) can optionally be solely a sulfur scavenger component, the combination of an oxidation catalyst and a sulfur scavenging component or the admixture of a lean NO<sub>x</sub> catalyst and sulfur scavenging component.

The sulfur scavenging component requires regenerations that are achieved by rich excursions either in a continuous or in a periodic way. The duration of the regenerations is depending on the adopted maintenance strategy, and tuned to create both sufficient richness and sufficient exotherm over the sulfur trap (3) to cause sulfur release. Where the trapping efficiency of sulfur scavenging components can be mapped, regeneration requirements can be established on a time basis, or, optionally, a sensor can be employed to determine when sulfur purges must be achieved. For example, the sulfur trap is operated at temperatures up to about 600°C or so, and typically about 150°C - 550°C, with lean/rich modulations at appropriate intervals to maintain the desired sulfur removal from the exhaust stream, i.e., a continuous regeneration

mode. Generally, the lean cycle is up to about 300 seconds(s) or so, with about 10 to about 250 seconds preferred, and about 30 to about 240 seconds especially preferred. Meanwhile, the rich cycle is up to about 15 seconds or so, with up to about 10 seconds preferred, and about 1 to about 5 seconds especially preferred  
5 (see Figure 18, illustration of a continuous regeneration). Lean/rich modulations can be achieved via an in cylinder fuel injection (2A) or via an in exhaust injection (2B), as illustrated in Figure 16 and 17.

The beneficial effects gained by inclusion of the sulfur trap within an exhaust system may be seen by monitoring the resulting improved  
10 NO<sub>x</sub> adsorption efficiencies and NO<sub>x</sub> conversion efficiencies. Reference is made to Figs. 14 and 15, where each Figure shows improved adsorption and conversion performance using the sulfur trap (lines 132 and 142, respectively) relative to the performance of a NO<sub>x</sub> adsorber in an exhaust system lacking the sulfur trap (lines 131 and 141, respectively). NO<sub>x</sub> adsorption was measured at  
15 300°C, and adsorption and conversion efficiencies were measured on NO<sub>x</sub> adsorbers after 30 hours of modulation aging with 10 ppm SO<sub>2</sub> at 400°C.

Though the sulfur species expelled during regeneration generally must travel through the NO<sub>x</sub> adsorber in the underfloor position, such species only do so during higher temperature phases and in a rich exhaust atmosphere.  
20 Sulfur poisoning of the NO<sub>x</sub> adsorber is thus reduced over operating time.

On the other hand, where the sulfur scavenging component is not used, sulfur poisoning is far more detrimental, since sulfur species are present in the exhaust stream during lean periods and at lower temperatures. In light of this contrast, it is easily recognized that by using the present invention, high  
25 efficiency duration of a NO<sub>x</sub> adsorber in an underfloor position can be considerably increased.

The exhaust gas catalyst system having high sulfur storage capacity across a range of temperatures and A/F ratios, and effective prevention of NO<sub>x</sub> adsorber sulfur poisoning while providing additional catalytic  
30 components, will preferably be located in a close coupled position. The sulfur trap provides high sulfur protection maintained via periodic or continuous



regenerations, and good durability in trapping efficiencies despite aging and regenerations along with multifunctional properties, allowing for substantive performance in sulfur adsorption, warm-up catalytic activity, and lean NO<sub>x</sub> catalysis. Further, as for the NO<sub>x</sub> adsorber in an underfloor position, utilization  
5 of sulfur protection significantly extends NO<sub>x</sub> adsorber high-activity periods. Consequently, NO<sub>x</sub> adsorber desulfurization is rarely required, translating to better fuel economy.

The sulfur trap presented in Figure 20, which is suitable for a periodic regeneration strategy, can comprise, for example, any sulfur scavenging  
10 components including, but not limited to, Ag, Zn, Ce, Co, Ba, Mg, and the like, noble metals including, but not limited to, Pd, Rh, and the like, and of support including alumina and titania, and the like, as well as mixtures comprising at least one of the foregoing materials. The sulfur trap presented in Figure 21, which is suitable for continuous regeneration strategy, can comprise, for  
15 example, any sulfur scavenging components including, but not limited to, Ag, Zn, Ba, Sr, and the like, noble metal catalysts including Pt, Pd, Rh, and support including alumina, titania and zeolite, and the like, as well as mixtures comprising at least one of the foregoing materials.

Figure 24 is a projection of sulfur trap regeneration frequency as  
20 a function of sulfur content in the fuel, in the case of a periodic regeneration strategy (which incorporates average speed, space velocities and similar assumptions). For the best sulfur trap, at 10ppm sulfur in the fuel, a regeneration of the sulfur trap would be required about every 5,000 miles only. If the NO<sub>x</sub> adsorber downstream from the sulfur trap survives 10 regenerations  
25 of the sulfur trap before it needs a desulfurization itself, then the NO<sub>x</sub> adsorber desulfurization will be required about every 50,000 miles, with NO<sub>x</sub> adsorber desulfurization required whenever the NO<sub>x</sub> conversion ratio falls below the required level (e.g., about 60%, 70%, 80%, or more, depending on the application). On the other end, a calculation based similar approximations  
30 shows that the current generation of NO<sub>x</sub> adsorber would be completely

deactivated (i.e., would provide 0% NO<sub>x</sub> conversion), after 28,000 miles of driving with a fuel containing 10 ppm of sulfur.

Other advantages include the fact that the sulfur trap functions at start-up, and functions to remove hydrocarbons and NO<sub>x</sub> (due to the presence of the NO<sub>x</sub> and oxidation catalysts), thereby substantially eliminating a light-off penalty. See Figure 15 which shows that after severe aging (e.g., an engine aging with a sequence of 4 minutes at A/F 14 (rich), 8 minutes at A/F 14.56 (stoichiometric), 20 seconds at A/F 18.2 ) at 995°C for 100 hours, the light-off performance is not affected by the incorporation of a sulfur trap.

While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention. Accordingly, it is to be understood that the present invention has been described by way of illustration and not limitation.

## CLAIMS

1. An exhaust gas catalyst system, comprising:  
a sulfur trap disposed within an exhaust stream, said sulfur trap comprising a sulfur scavenger component; and  
a NO<sub>x</sub> adsorber catalyst disposed within the exhaust stream,  
5 downstream from said sulfur trap.
2. The exhaust gas catalyst system of Claim 1, wherein said sulfur scavenging component is an inorganic material having an affinity for sulfur species such that said sulfur scavenging component traps sulfur components within an exhaust stream flowing over said sulfur scavenging  
5 component.
3. The exhaust gas catalyst system of Claim 2, wherein said sulfur scavenging component is a trapping element selected from the group consisting of Ag, Al, Ba, Ce, Co, Cu, La, Li, Mg, Nd, Rb, Sn, Sr, Zn, and mixtures and alloys comprising at least one of the foregoing trapping elements.
4. The exhaust gas catalyst system of Claim 1, wherein said sulfur scavenging component is loaded on a porous support selected from the group consisting of alumina, gamma-alumina, alpha-alumina, zeolite, zirconia, ceria, magnesium oxide, titania, silica, and mixtures comprising at least one of  
5 the foregoing supports.
5. The exhaust gas catalyst system of Claim 1, further comprising an oxidation catalyst.
6. The exhaust gas catalyst system of Claim 5, wherein said oxidation catalyst is selected from the group consisting of platinum, palladium, rhodium, and mixtures comprising at least one of the foregoing catalysts.

7. The exhaust gas catalyst system of Claim 1, further comprising a lean NO<sub>x</sub> catalyst.

8. The exhaust gas catalyst system of Claim 7, wherein said lean NO<sub>x</sub> catalyst comprises: a support selected from the group consisting of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and mixtures comprising at least one of the foregoing supports; one or more zeolitic materials; and one or more precious  
5 metals.

9. The exhaust gas catalyst system of Claim 1, further comprising a three-way catalyst positioned downstream of the NO<sub>x</sub> adsorber or within the NO<sub>x</sub> adsorber washcoat.

10. The exhaust gas catalyst system of Claim 1, further comprising a particulate filter, housed in an underfloor position, upstream of said NO<sub>x</sub> adsorber.

11. The exhaust gas catalyst system of Claim 1, further comprising a sulfur trap bypass valve for spraying injected fuel directly in front of said NO<sub>x</sub> adsorber.

12. The exhaust gas catalyst system of Claim 11, further comprising a particulate filter, housed in an underfloor position, upstream of said NO<sub>x</sub> adsorber.

13. The exhaust gas catalyst system of Claim 1, further comprising a three-way valve, between the sulfur trap and the NO<sub>x</sub> adsorber, for diverting a short, rich exhaust period around said NO<sub>x</sub> adsorber catalyst.

14. The exhaust gas catalyst system of Claim 13, further comprising a particulate filter, housed in an underfloor position, upstream of said NO<sub>x</sub> adsorber.

15. The exhaust gas catalyst system of Claim 1, wherein said sulfur trap is housed in a close-coupled position relative to an internal combustion engine.

16. A method of reducing sulfur poisoning of a nitrogen oxide adsorber, housed within an exhaust gas catalyst system, comprising:  
placing a sulfur trap within the exhaust stream upstream from a NO<sub>x</sub> adsorber, housed in an underfloor position, wherein said sulfur trap

5 comprises: a sulfur scavenger component;

removing sulfur species from said exhaust stream into said sulfur trap according to the sulfur affinity of said sulfur scavenger component; and

directing the resulting exhaust stream, having a reduced sulfur species concentration, to said NO<sub>x</sub> adsorber.

17. The method of Claim 16, wherein said sulfur scavenging component is an inorganic material having an affinity for sulfur species such that said sulfur scavenging component traps sulfur components within an exhaust stream flowing over said sulfur scavenging component.

18. The method of Claim 17, wherein said sulfur scavenging component comprises a trapping element selected from the group consisting of Ag, Al, Ba, Ce, Co, Cu, La, Li, Mg, Nd, Rb, Sn, Sr, Zn, and mixtures and alloys comprising at least one of the foregoing trapping elements.

19. The method of Claim 16, wherein said sulfur scavenging component is loaded on a porous support selected from the group consisting of alumina, gamma-alumina, alpha-alumina, zeolite, zirconia, ceria, magnesium oxide, titania, silica, and a mixture comprising at least one of the foregoing supports.

20. The method of Claim 16, wherein said sulfur trap further comprises an oxidation catalyst.

21. The method of Claim 20, wherein said oxidation catalyst is selected from the group consisting of platinum, palladium, rhodium, and mixtures and alloys comprising at least one of the foregoing catalysts.

22. The method of Claim 16, wherein said sulfur trap further comprises a lean NO<sub>x</sub> catalyst.

23. The method of Claim 22, wherein said lean NO<sub>x</sub> catalyst comprises: a support selected from the group consisting of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and mixtures comprising at least one of the foregoing supports; one or more zeolitic materials; and one or more precious metals.

24. The method of Claim 16, wherein the exhaust gas catalyst system further comprises a three-way catalyst positioned downstream of the nitrogen oxide adsorber or within the NO<sub>x</sub> adsorber washcoat.

25. The method of Claim 16, further comprising spraying injected fuel directly in front of said NO<sub>x</sub> adsorber via a bypass valve such that oxygen is consumed on said NO<sub>x</sub> adsorber prior to exposure to a sulfur rich pulse.

26. The method of Claim 25, further comprising filtering particulate materials from said exhaust stream via a particulate trap, housed between the sulfur trap and the NO<sub>x</sub> adsorber.

27. The method of Claim 26, wherein spraying fuel directly in front of said NO<sub>x</sub> via said bypass valve occurs during regeneration of said particulate trap.

28. The method of Claim 16, further comprising diverting a short, fuel-rich exhaust pulse around said NO<sub>x</sub> adsorber catalyst via a three-way valve, located between the sulfur scavenging component and said NO<sub>x</sub> adsorber prior to exposure of said NO<sub>x</sub> adsorber to a sulfur rich pulse.

29. The method of Claim 28, further comprising filtering particulate materials from said exhaust stream via a particulate trap, housed between the sulfur trap and the NO<sub>x</sub> adsorber.

30. The method of Claim 29, wherein diverting said exhaust gas around said NO<sub>x</sub> adsorber by way of said three way valve to said NO<sub>x</sub> adsorber occurs immediately prior to regeneration of said particulate trap or of said sulfur trap warm-up catalyst.

31. The method of Claim 16, wherein said sulfur trap is housed in a close-coupled position relative to an internal combustion engine.

Figure 1

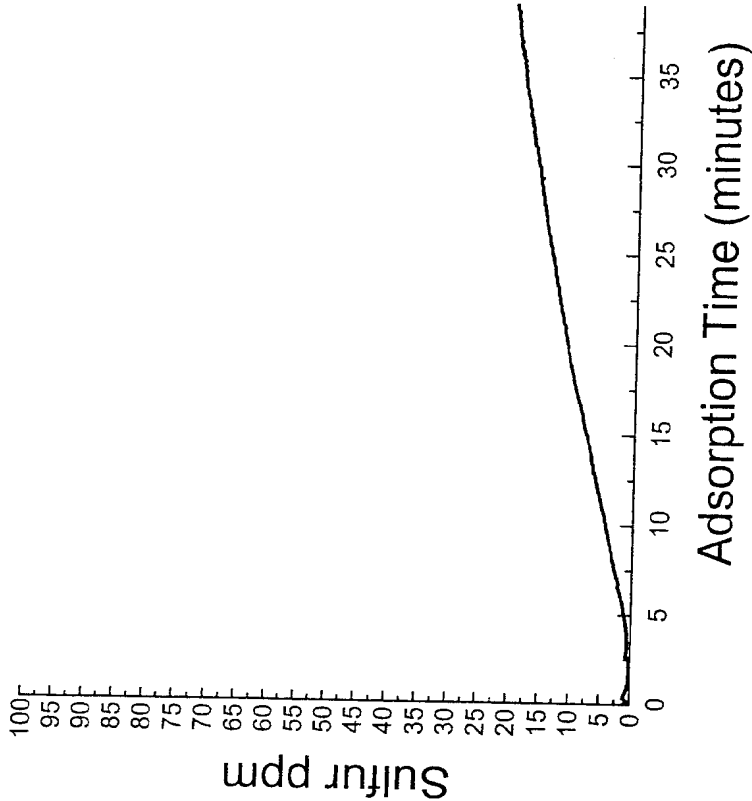


Figure 2

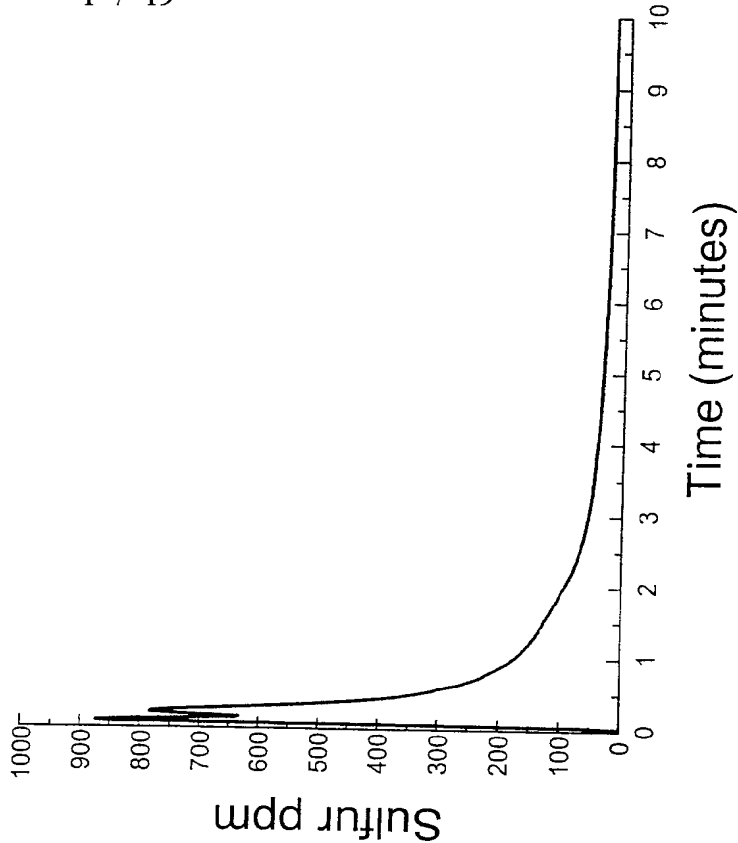




Figure 3

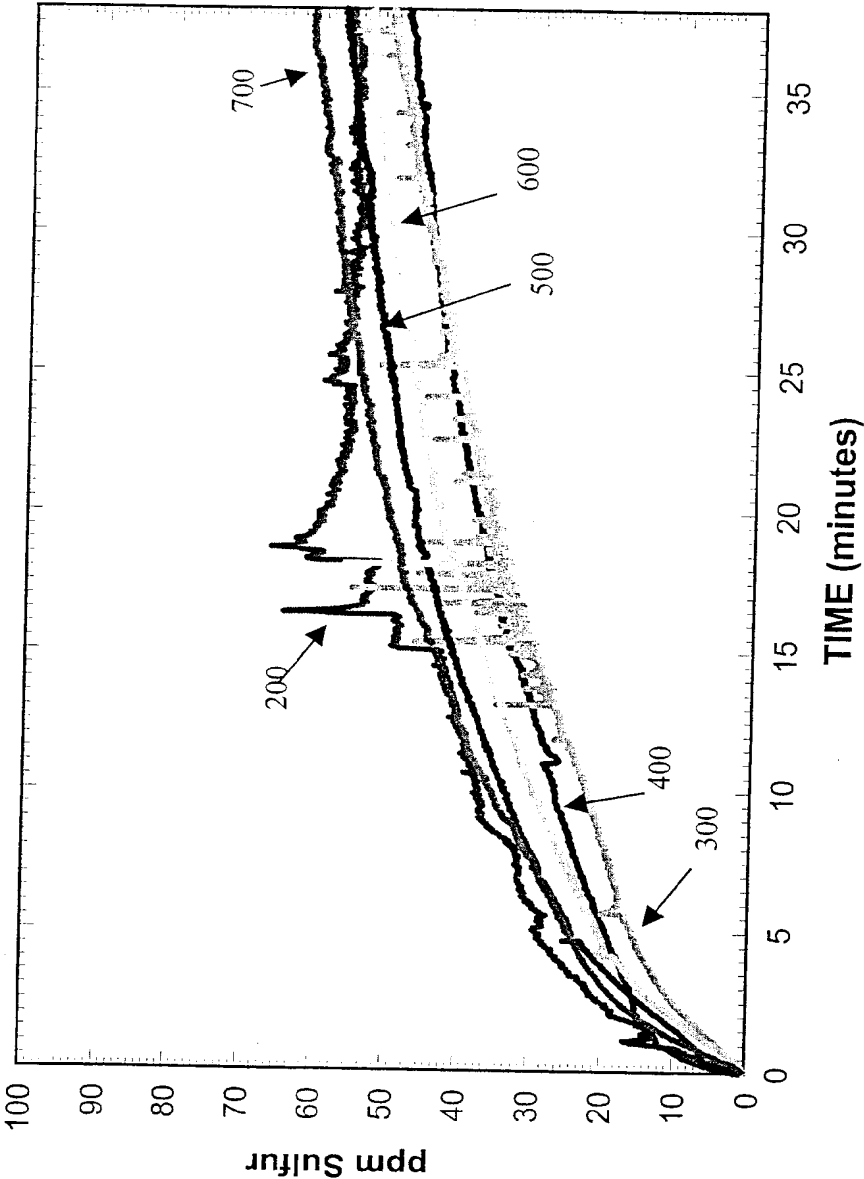


Figure 4

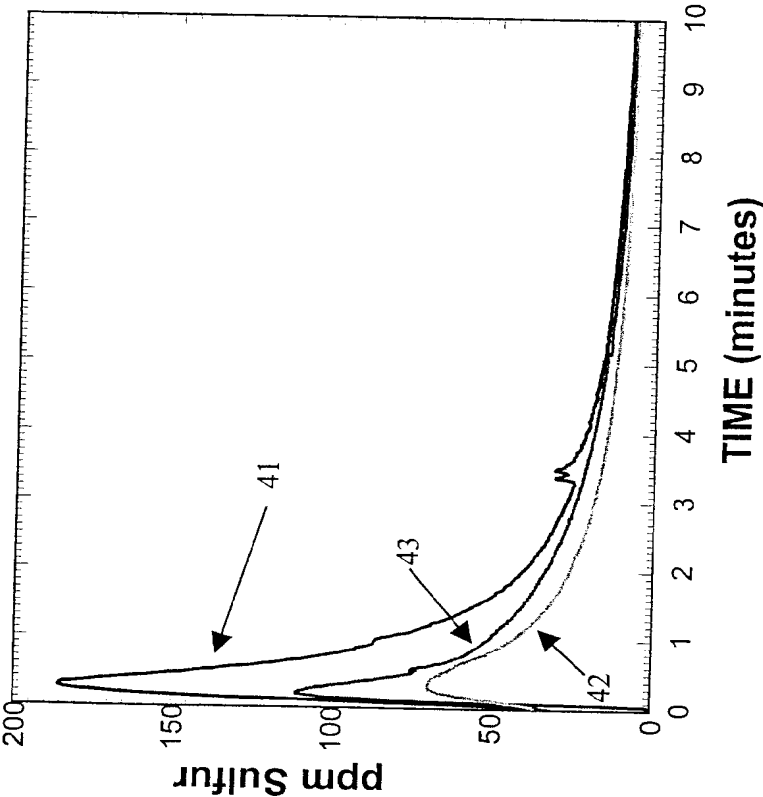


Figure 5

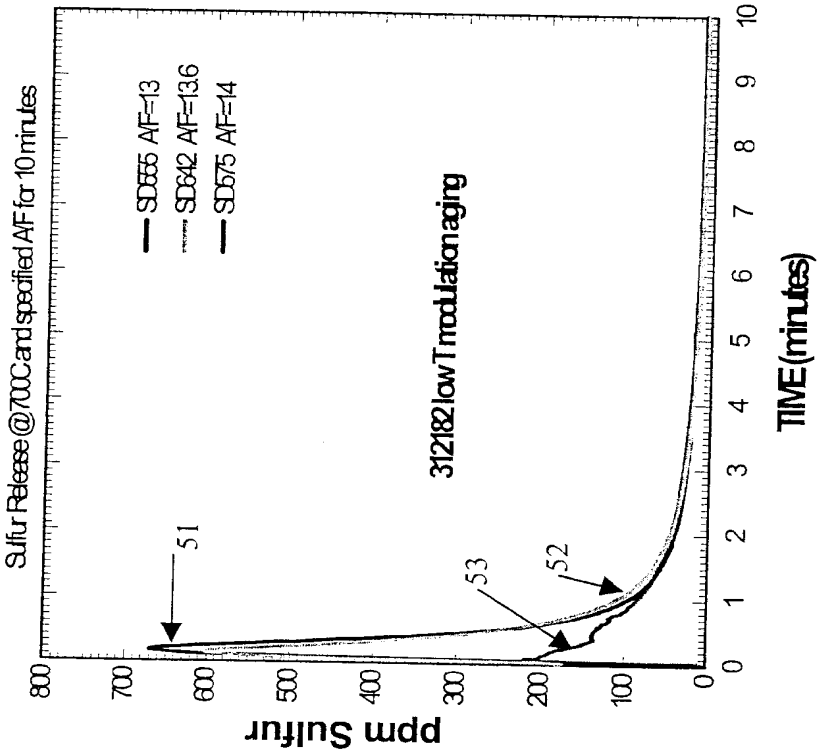


Figure 6

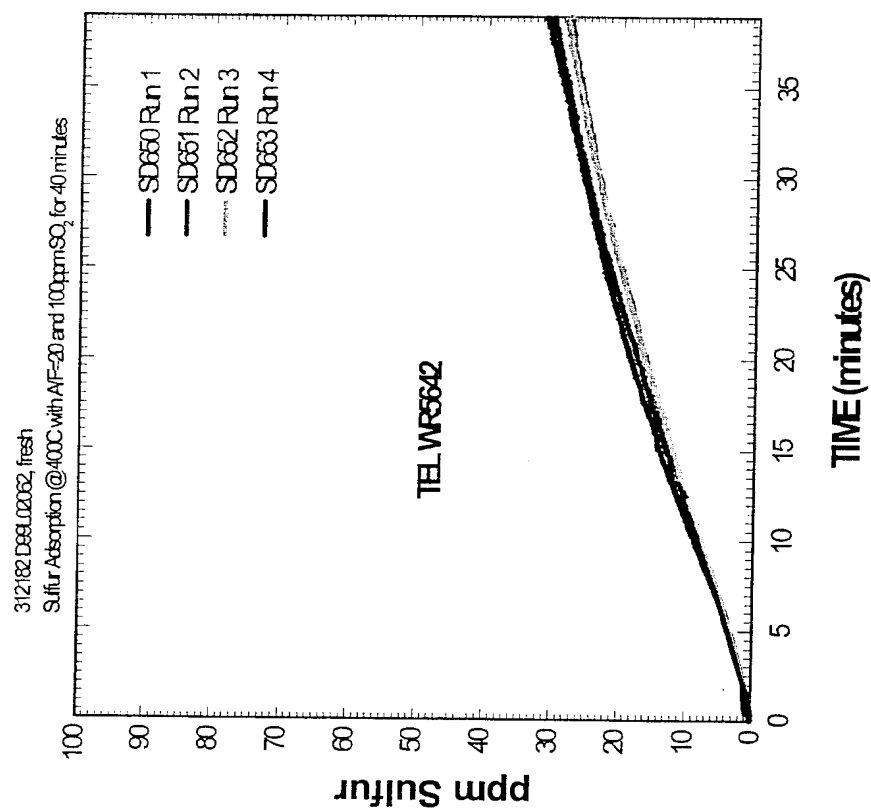


Figure 7

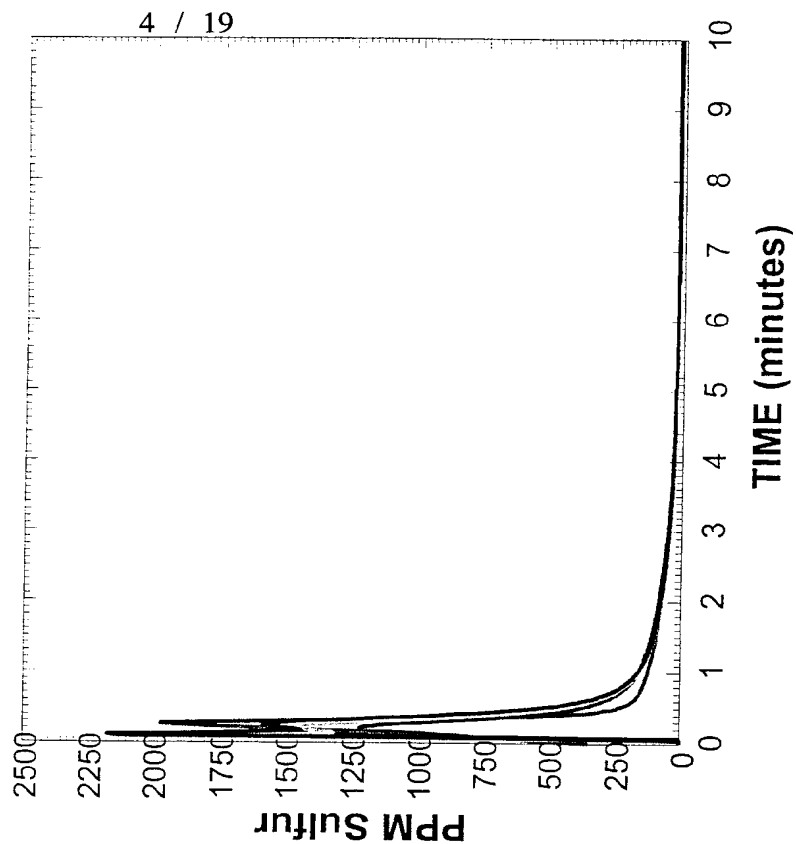


Figure 8

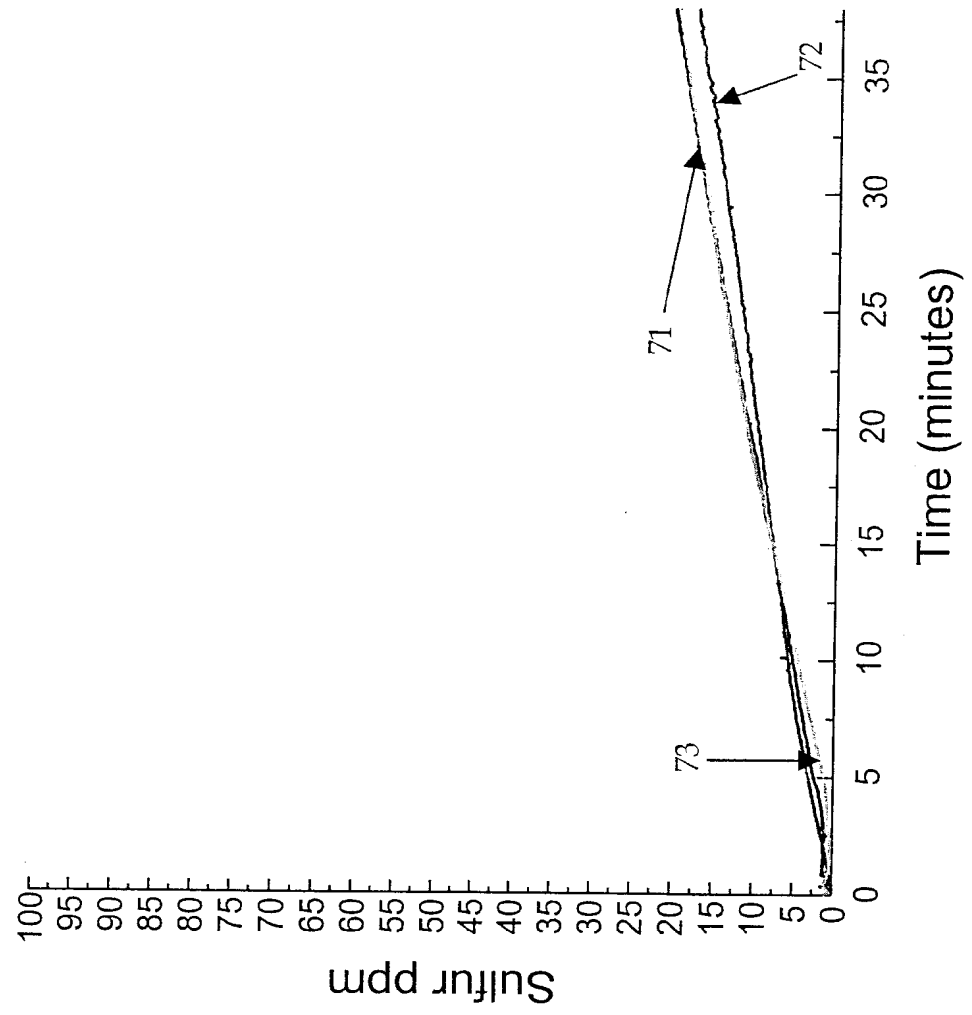


Figure 9

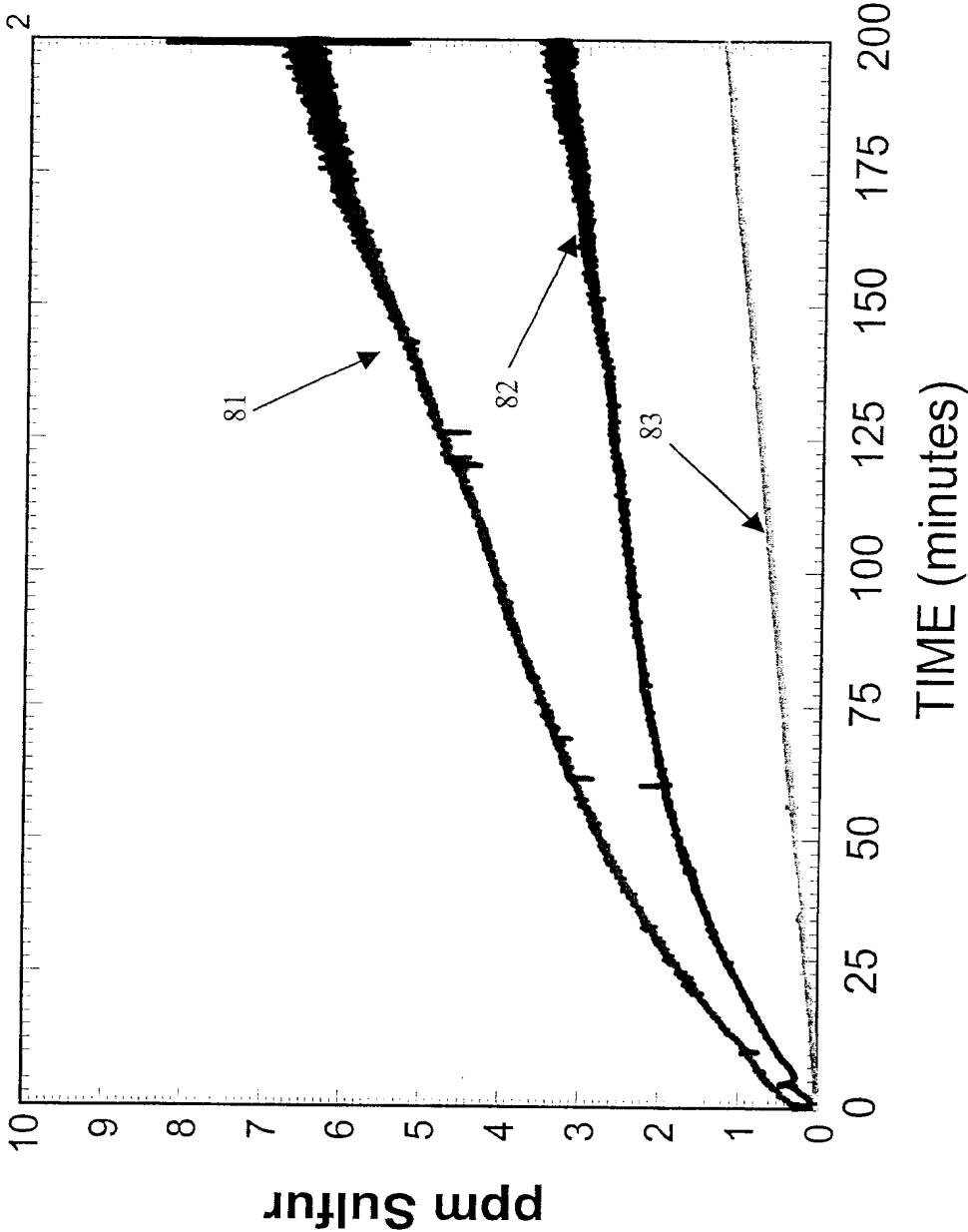


Figure 10

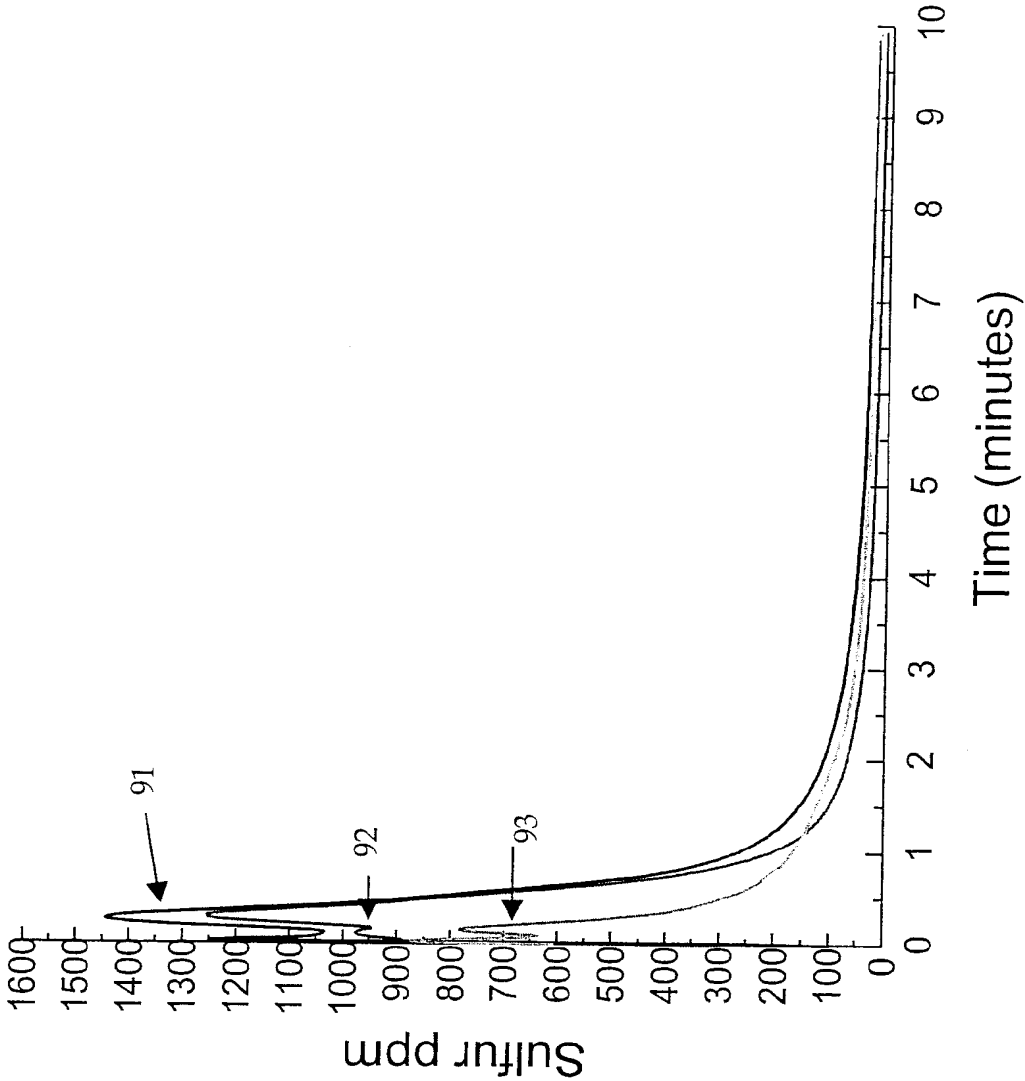


Figure 11

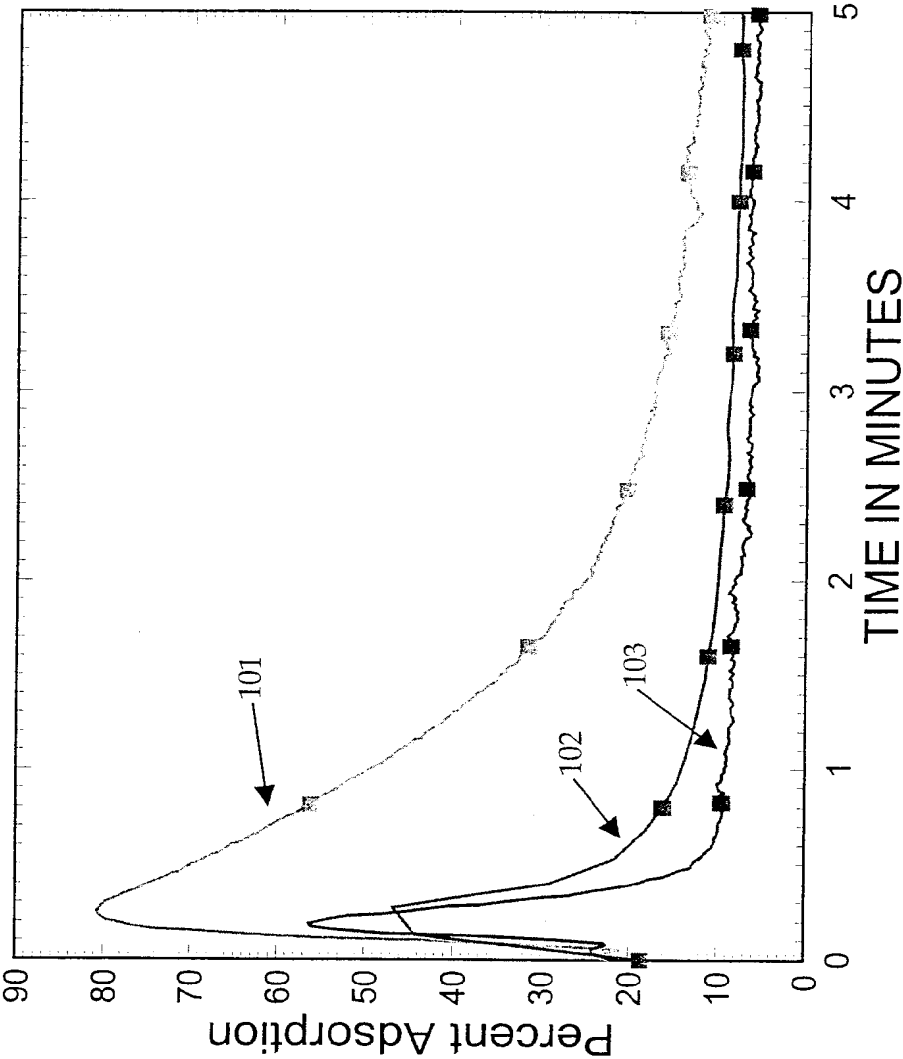


Figure 12  
NOx conversions

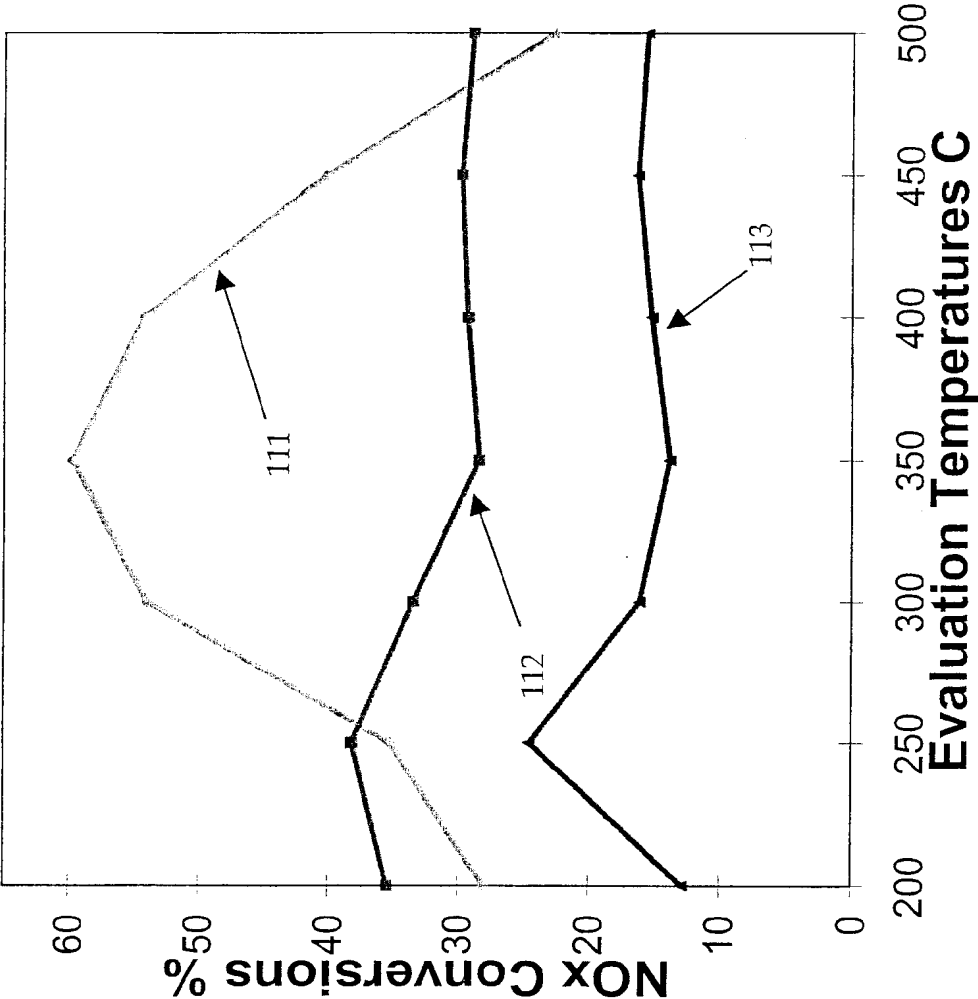




Figure 13

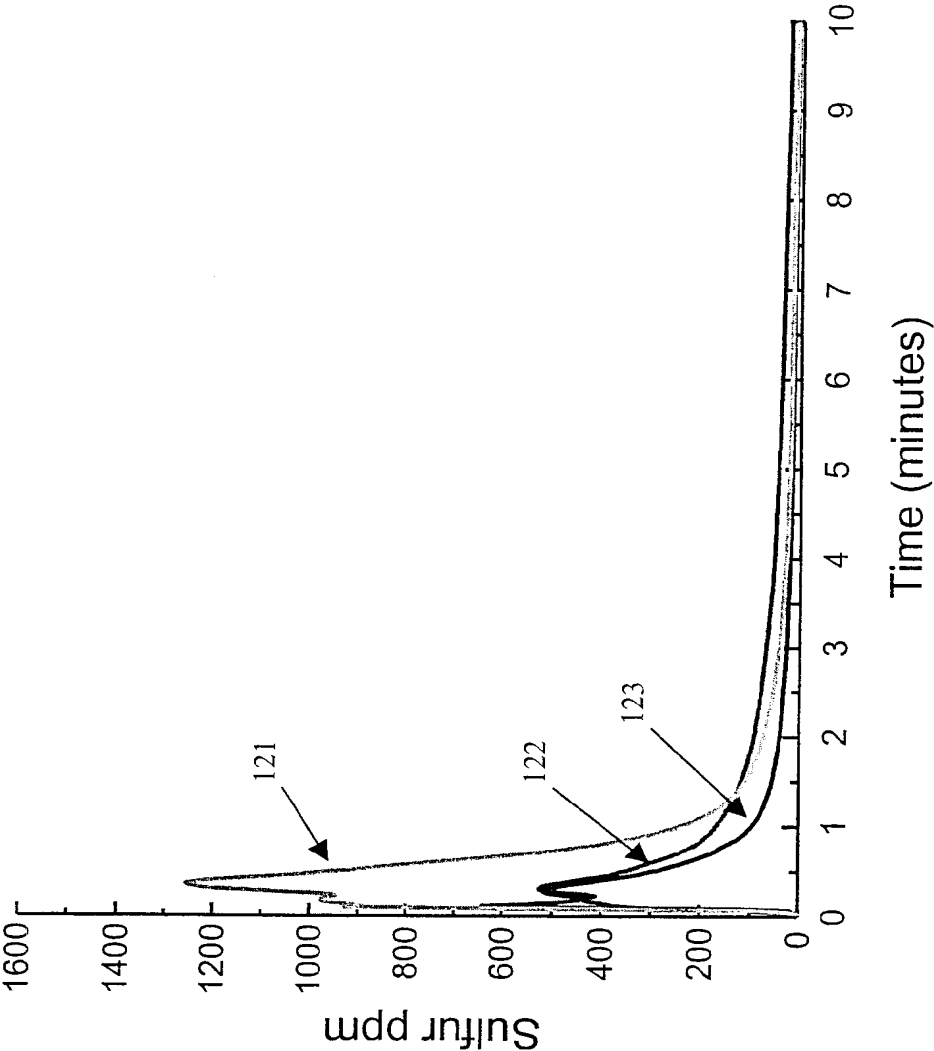


Figure 14

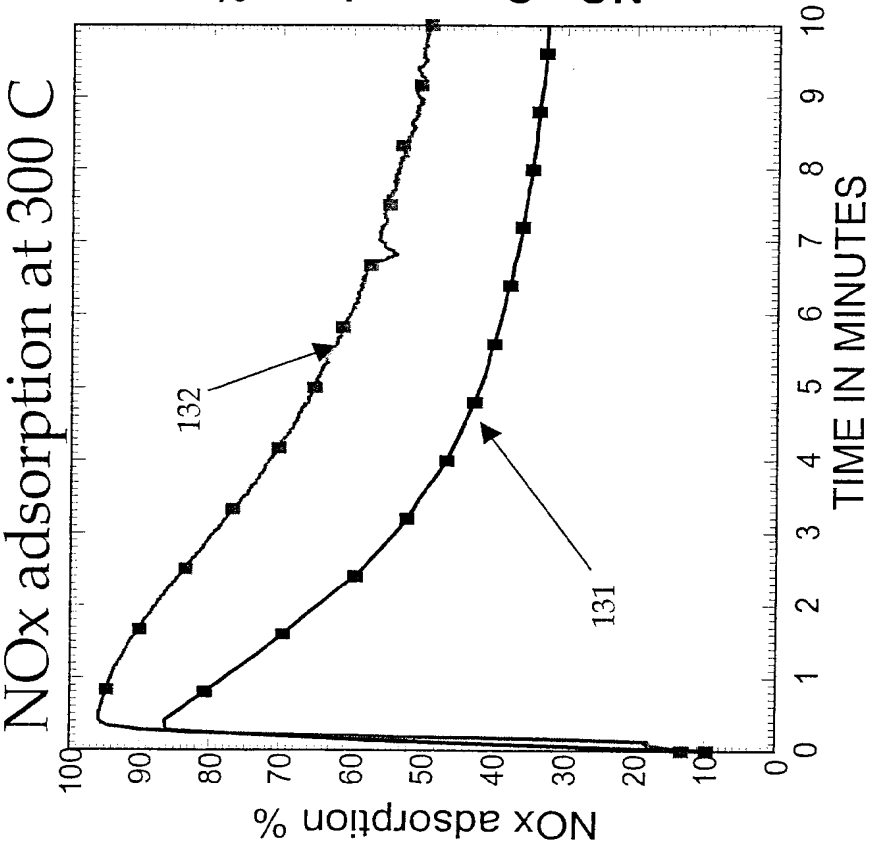
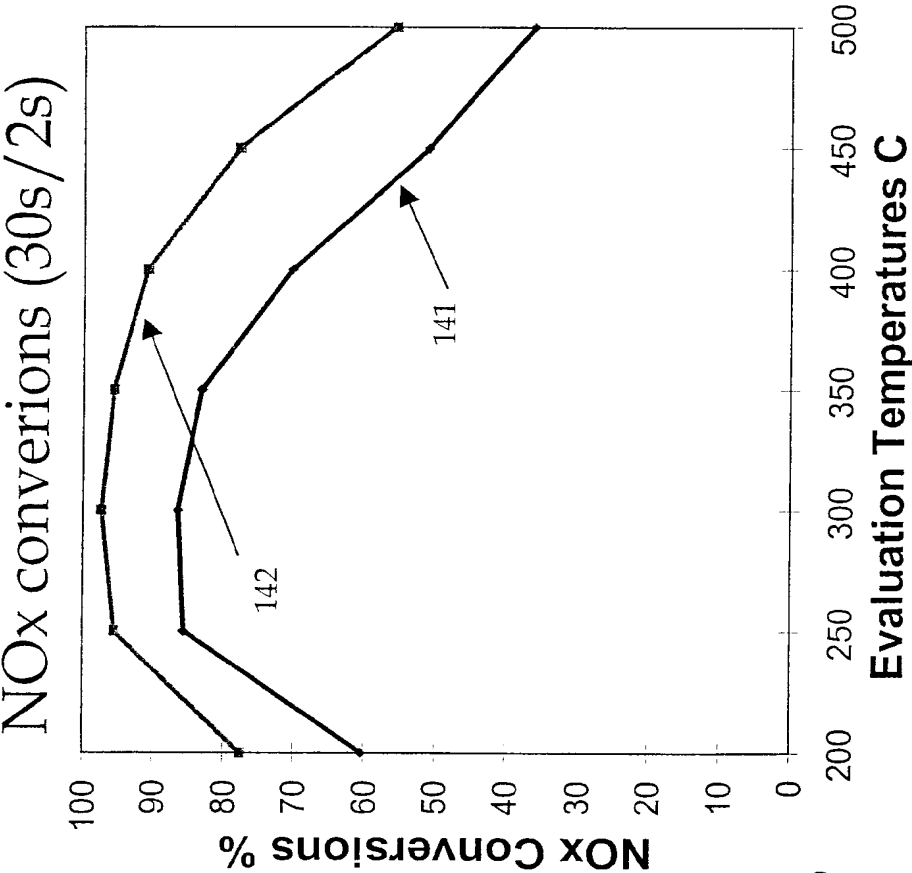


Figure 15



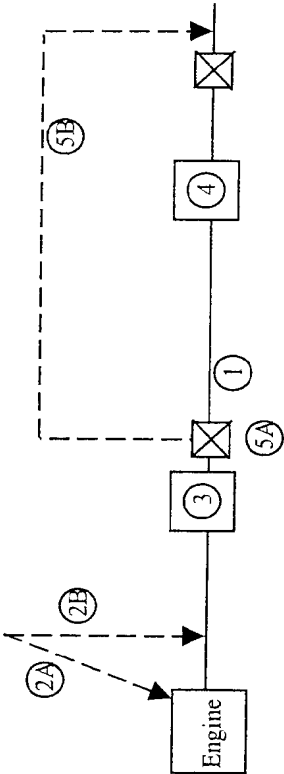


Figure 16

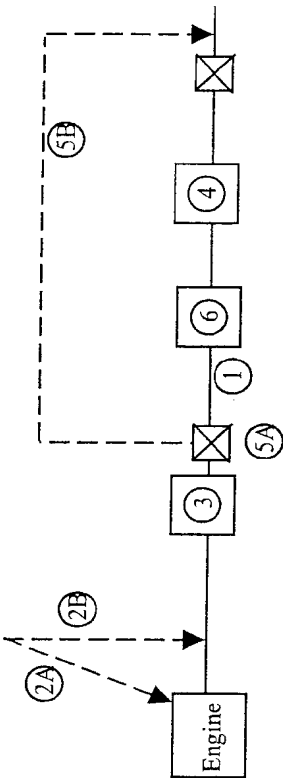
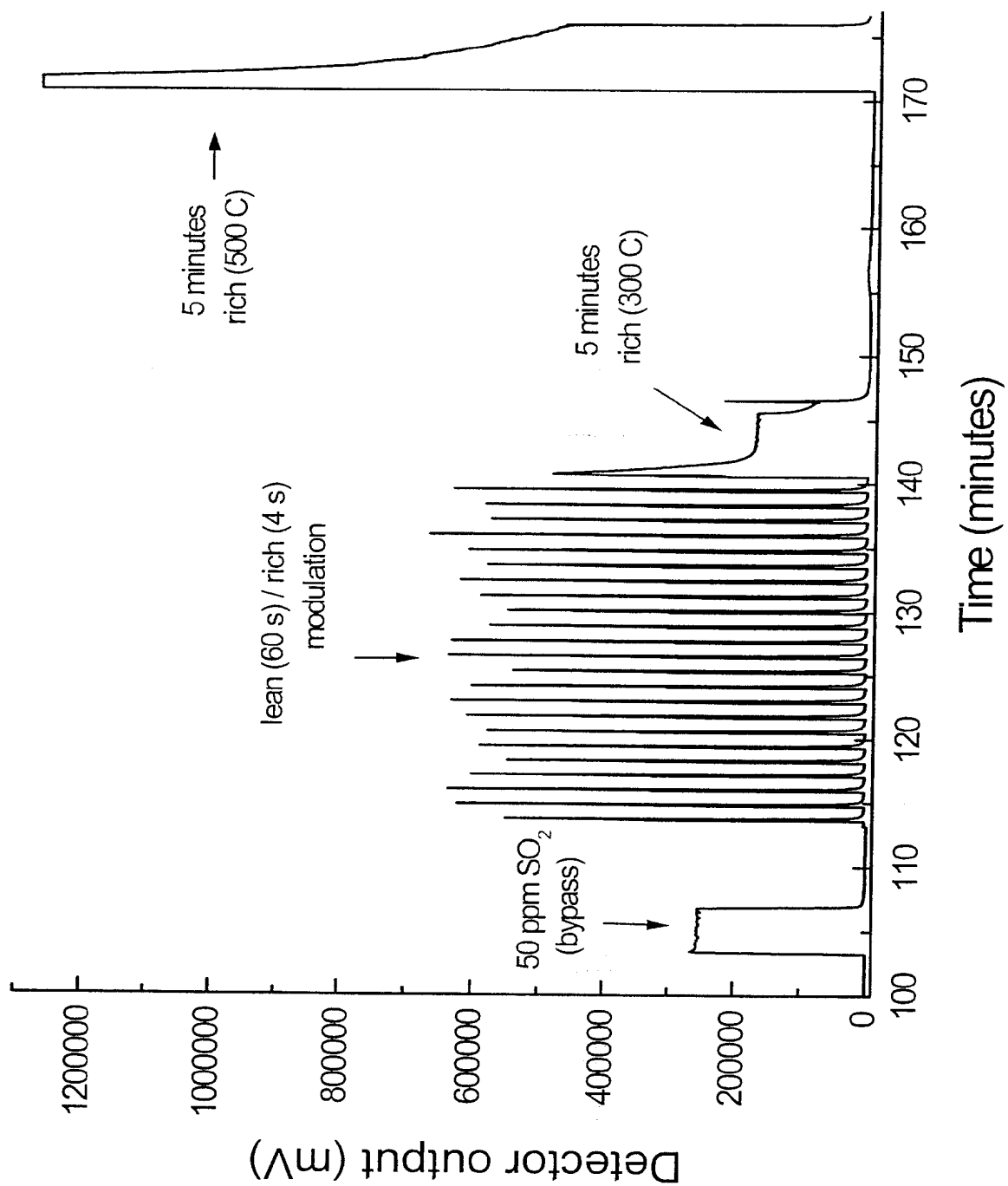


Figure 17

Figure 18



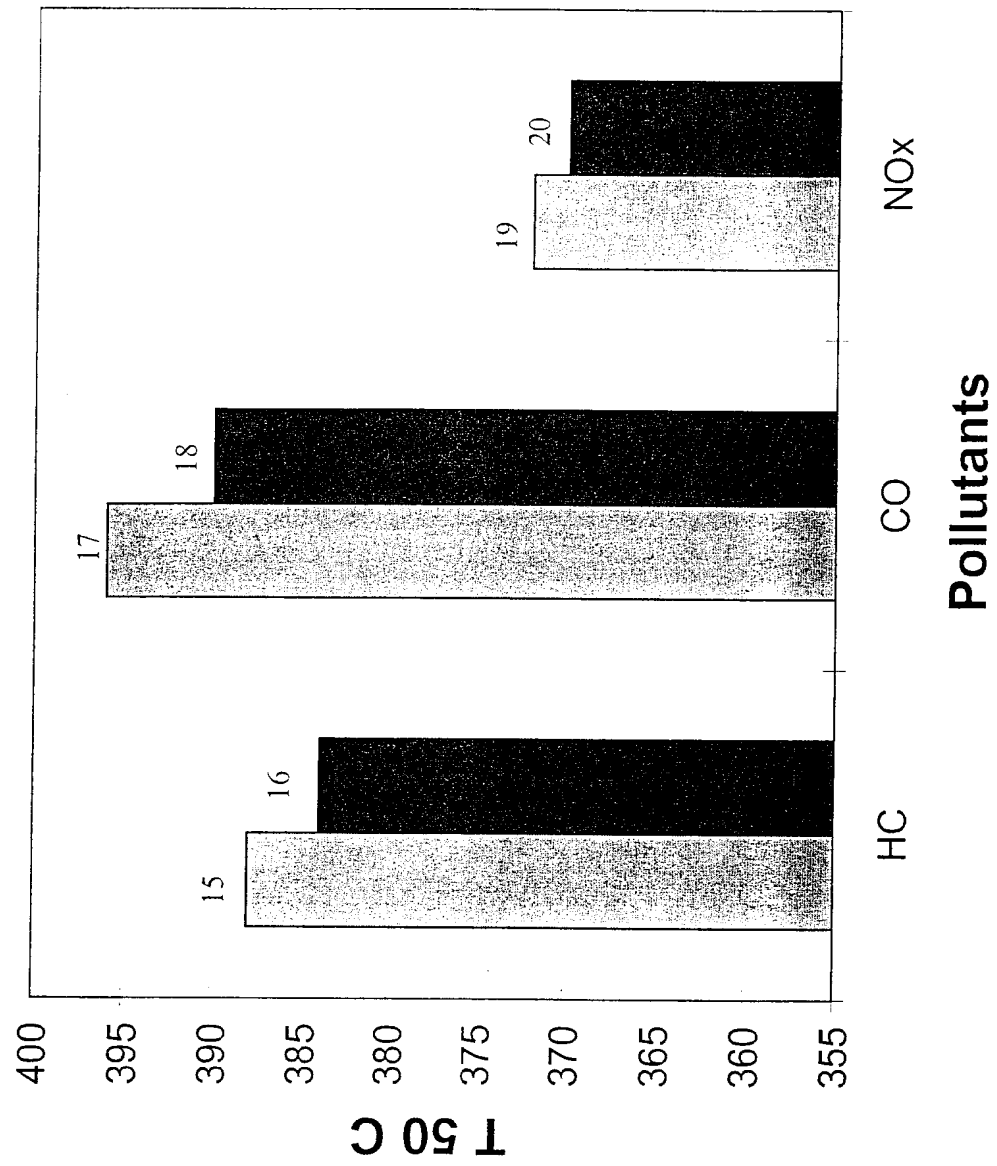
*Figure 19*

Figure 20

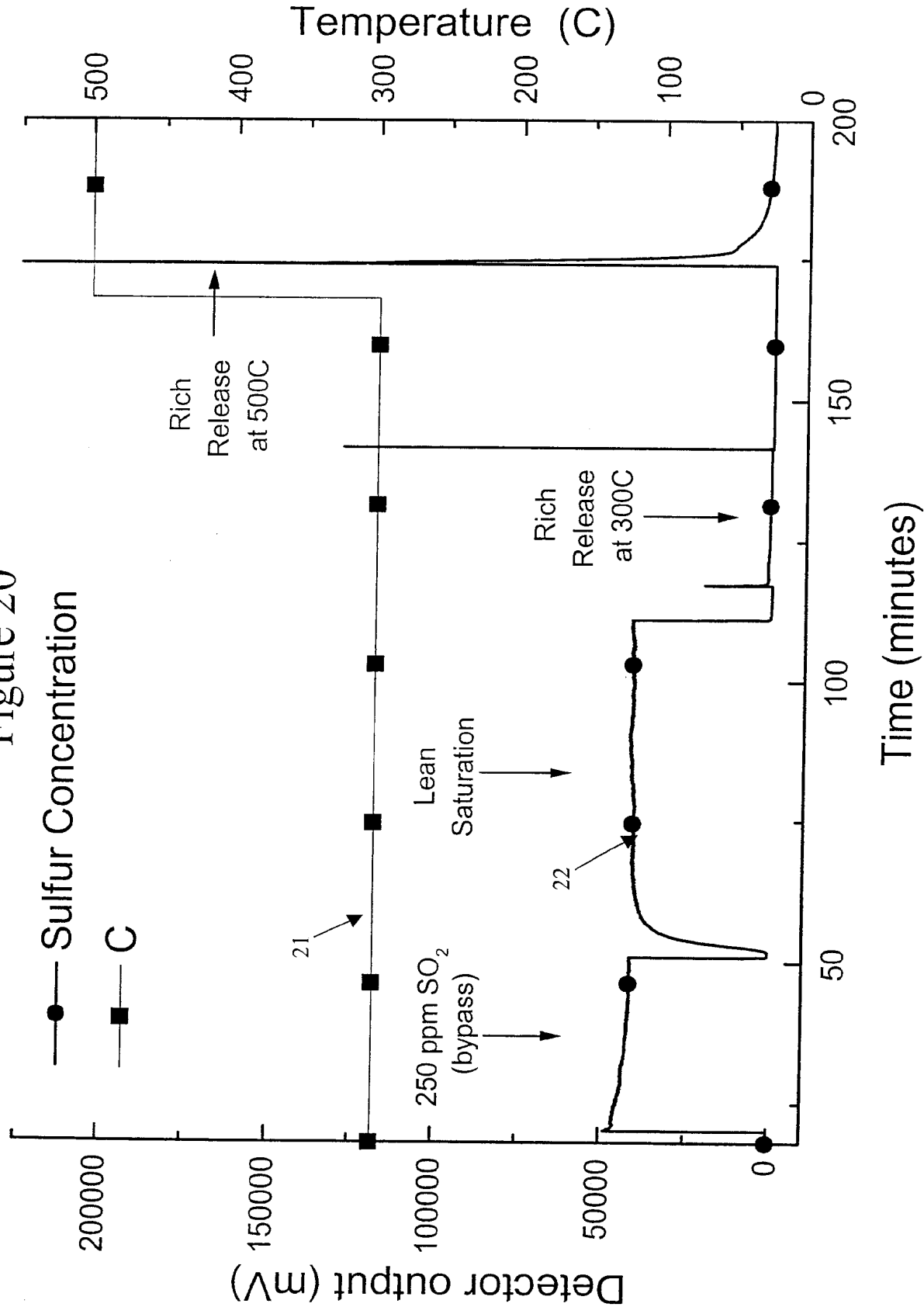


Figure 21

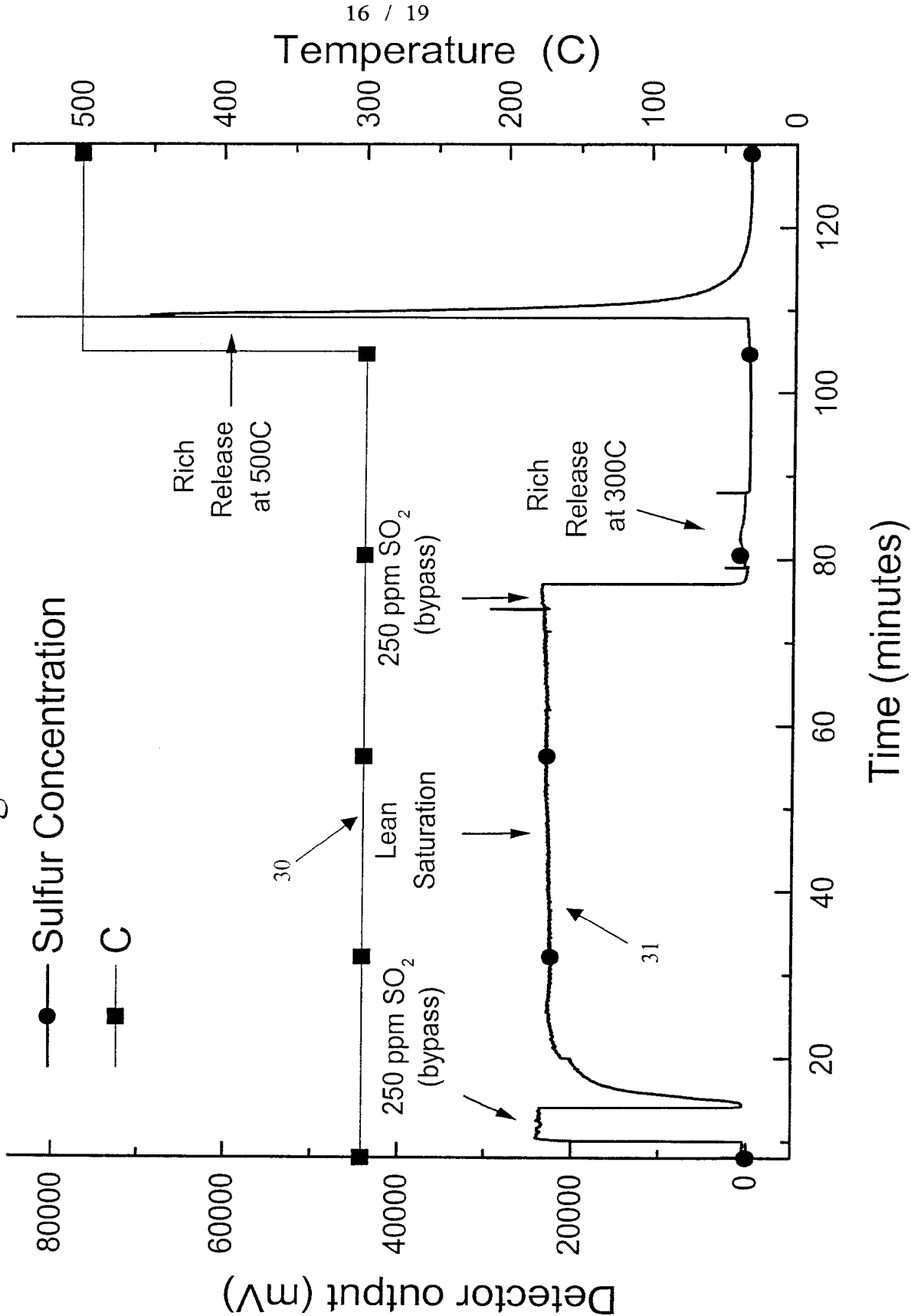


Figure 22

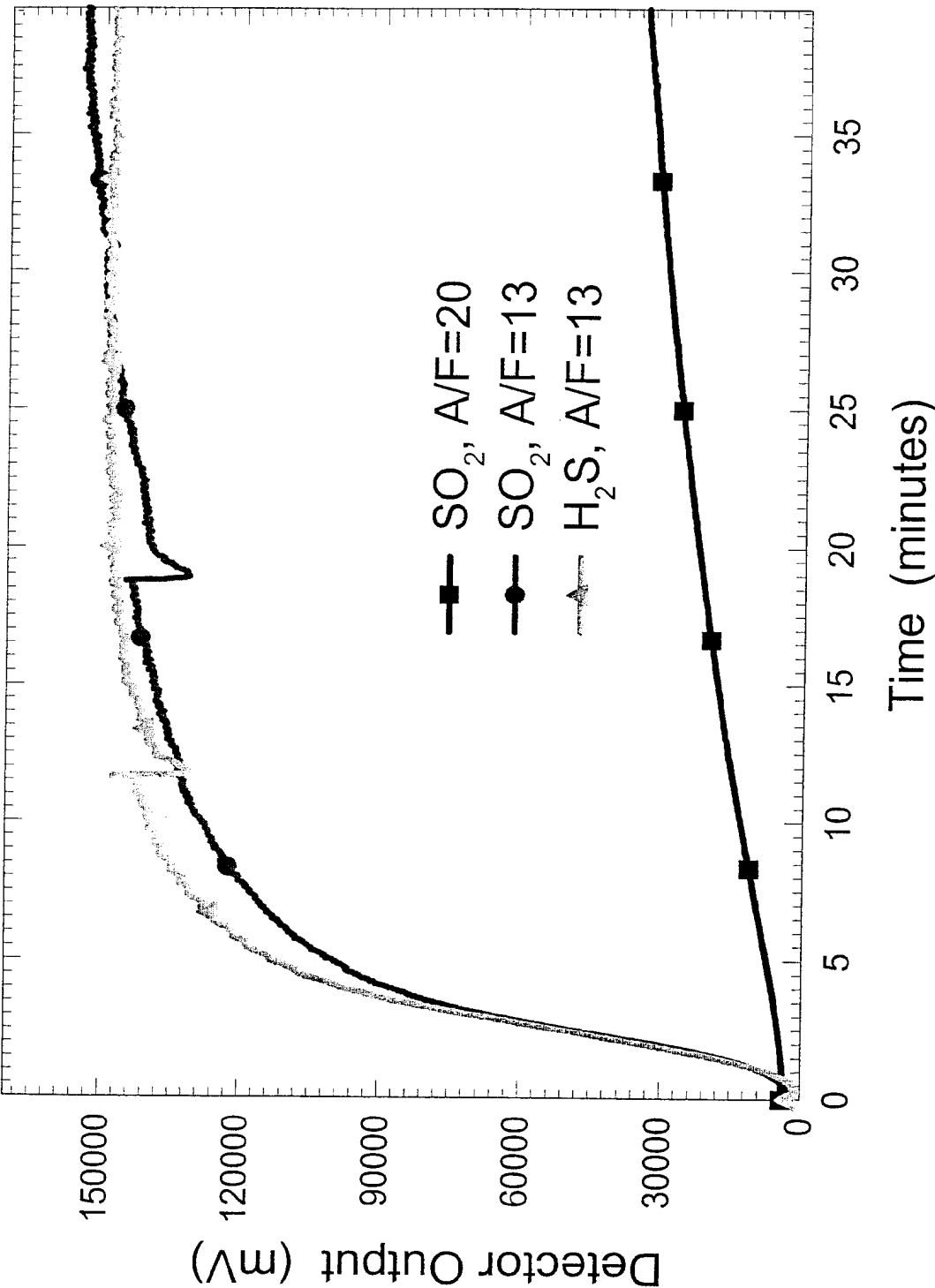




Figure 23

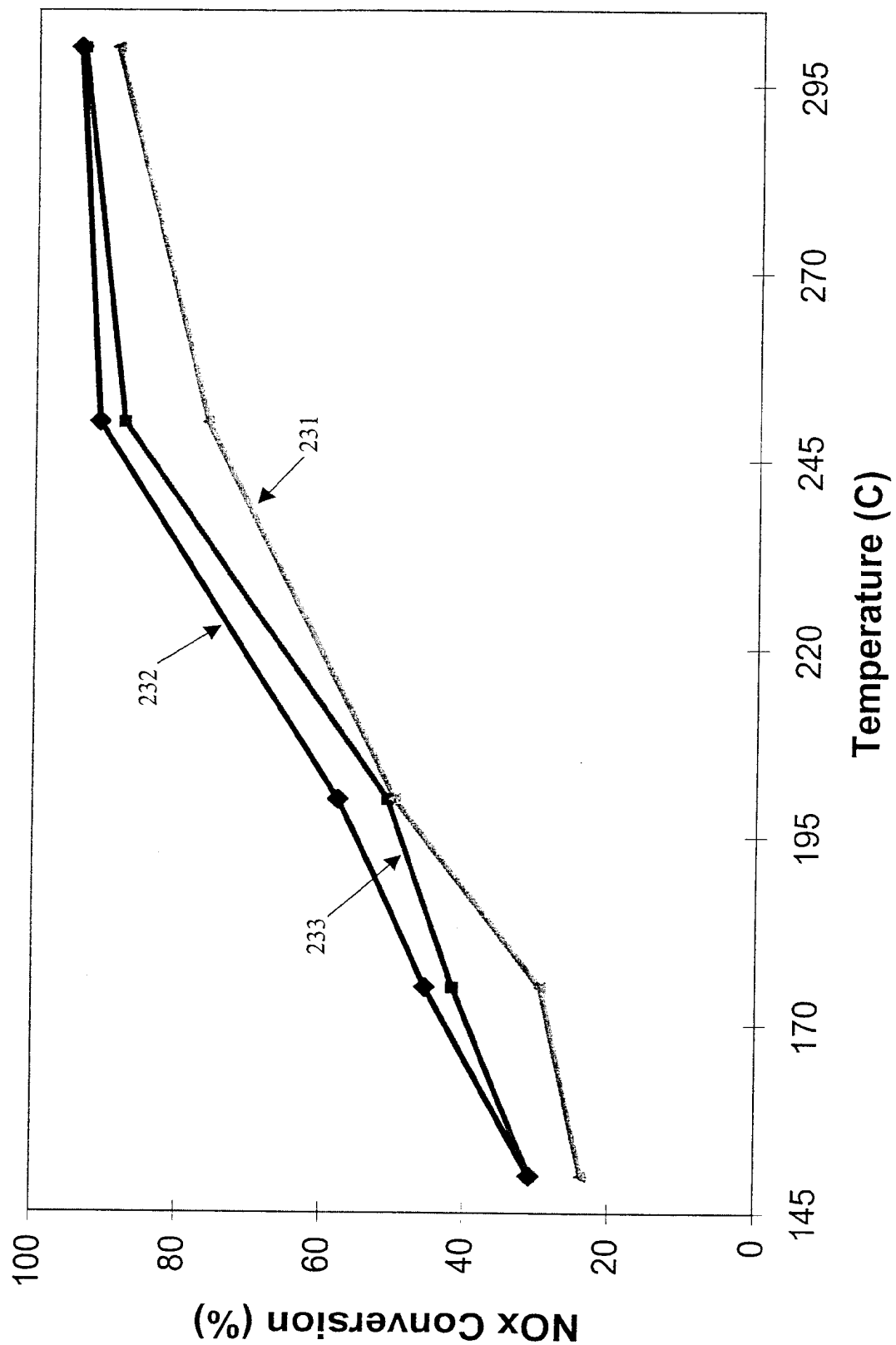
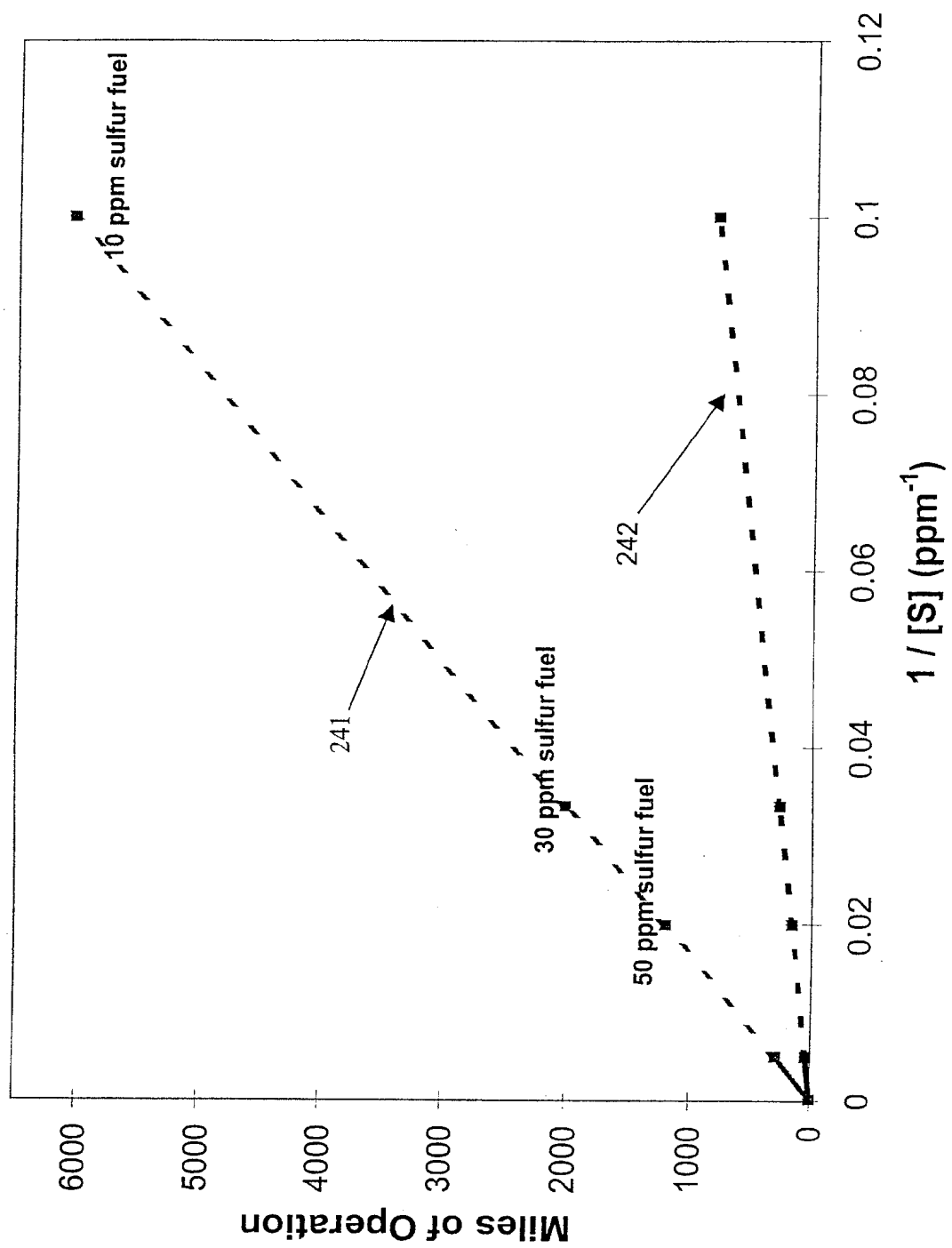


Figure 24



## INTERNATIONAL SEARCH REPORT

Internation Application No

PCT/US 01/02841

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01D53/94 F02D41/02 F01N3/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D F02D F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                    | Relevant to claim No.          |
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| X          | DE 197 53 573 A (BAYERISCHE MOTOREN WERKE)<br>10 June 1999 (1999-06-10)<br>the whole document<br>---<br><br>-/--                                                                                                                      | 1-9,<br>15-24,31               |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
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- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search

21 May 2001

Date of mailing of the international search report

30/05/2001

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Authorized officer

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# INTERNATIONAL SEARCH REPORT

Internation Application No  
PCT/US 01/02841

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category ° | Citation of document, with indication, where appropriate, of the relevant passages        | Relevant to claim No. |
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/02841

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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